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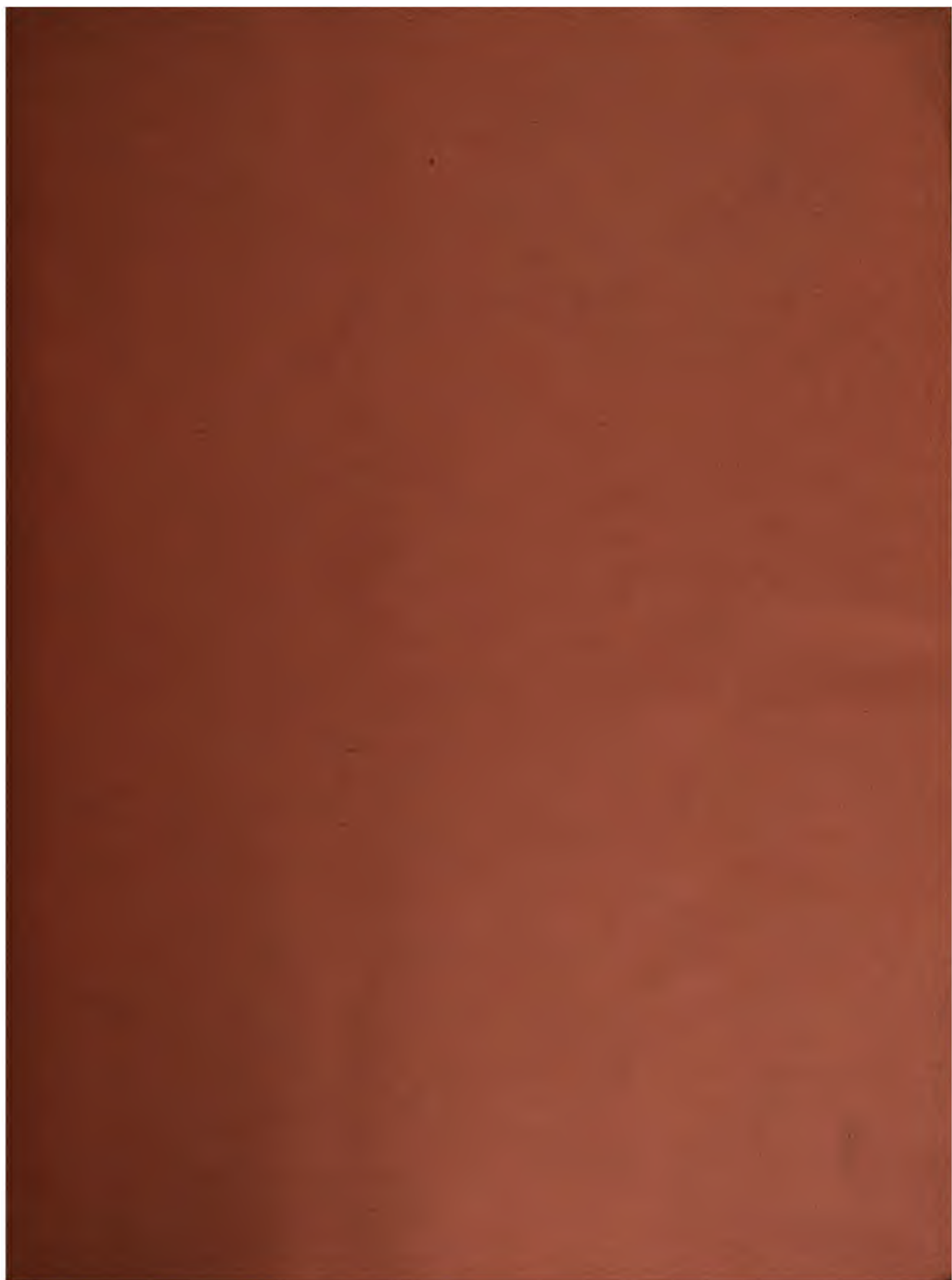
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SUPPLEMENT TO THE CHEMICAL NEWS, JULY 4, 1890.

THE
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IN ALL ITS APPLICATIONS TO
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THE CHEMICAL NEWS.

VOLUME LXI.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1571.—JANUARY 3, 1890.

THE LONG-CONTINUED ACTION OF THE ELECTRIC DISCHARGE ON IODINE.*

By C. LUEDEKING, Ph.D. (Leipzig).

SOME time ago, the author attempted the study of the effects of the electric discharge on iodine vapour, when continued over a long space of time. The researches of V. Meyer showed that with increasing temperature the vapour density of iodine becomes rapidly less than what is demanded by theory, finally reaching two-thirds of the theoretical value; a fact explained by the supposed partial dissociation of molecular into atomic iodine.

Later, J. J. Thomson (*Proc. Royal Soc.*, vol. xlii., pp. 343—345) showed that the silent discharge produces the same phenomena of anomalous densities that were observed by V. Meyer for higher temperatures. Several hours of time were necessary for the vapour to regain its normal density.

It was desired by the author to act upon the vapour of iodine, through a long period of time, by means of the electric discharge, and subject the result to analysis, with a view to establishing, if possible, any changes brought about.

Four Grove cells, of Browning's make, were used as electro-motive force. The circuit was passed through a Ruhmkorff coil, capable of giving sparks two inches long by this arrangement; the wires of the coil were connected with heavy platinum wires, sealed in a small heavy glass tube, with their ends opposite, and $\frac{1}{4}$ inch apart from one another. In this tube, 0.036 grm. of iodine was sealed hermetically. By gentle heat it was then vapourised, in part; the contents assuming the appearance of an intensely deep violet colour. The spark was now passed incessantly for three weeks, day and night, and the character of the light phenomena watched as carefully as possible. As the experiment advanced, the colour of the contents of the tube gradually changed, losing the rich deep violet tint that it had at first, very much resembling bromine vapour in appearance, and passing through this stage, becoming more and more faint, until, at the end of the afore-mentioned time, the tube was entirely colourless, and evidently all iodine had disappeared. What had become of it?

When reading Mr. C. P. Smyth's Address before the British Association, I recalled these experiments of mine, that had been made some time ago. His experiences are quite analogous to my own. In 1880, his iodine truly showed 148 iodine lines, and 3 exceedingly faint reproductions of the chief hydrogen lines; "Yet, in the present

year," he goes on to say, "there is not one iodine line left in that tube, and its spectrum range is filled with nothing but both high and low temperature hydrogen lines of astonishing brilliancy, while of the large amount of iodine granules hermetically sealed into the tube in 1878, only a very small amount of apparently inert dust is now left." Further, he states:—"Whether this change is an infinitesimally small part of the progress of everything to turn into hydrogen, and for assisting thereby the whole solar system to explode some day into a so-called and spectroscopically bright lined hydrogen star, I will by no means weary the Section by enquiring now."

It is clearly expressed that iodine has disappeared from a certain tube; that, whereas this tube contained at first only faint indications of hydrogen, it, after the disappearance of the iodine, showed the presence of this element in remarkable brilliancy or amount. The inference must be that iodine has been decomposed and that hydrogen is present as product of decomposition.

As our experimental results are similar in respect to disappearance of iodine, it will be of interest for me to describe my analytical manipulations of the contents of my iodine tube, and to show what my conclusions necessarily were.

As stated, the iodine had disappeared entirely from my tube. The platinum poles in the tube were much corroded and roughened; during the discharge, the ends were constantly at a bright red heat; the spark itself had a livid appearance, was uncertain in its course, changing frequently. The sides of the tube were affected as if by hydrofluoric acid, and there was in the tube what seemed to me also only a small amount of dust.

The tube was opened under water by nipping off the end; there was a partial vacuum, the water entering and filling it about one-fifth, by a rough estimate. I inferred at the time that the oxygen of the air, originally contained in the tube, had disappeared, and that what was left was nitrogen. This result is contrary to what we should expect had hydrogen been formed by dissociation of the iodine. The confined gases would have been under a pressure.

The contents of the tube were thoroughly extracted by water, the solution so obtained made slightly alkaline, and sulphuretted hydrogen passed to saturation. After expulsion of the gas, and slightly acidifying with nitric acid; nitrate of silver was added, and the precipitate filtered, washed, dried, and weighed. The quantity of precipitate produced was nearly equal to what theory requires for iodide of silver; it weighed 0.061 grm.

Evidently, then, in my experiment the disappearance of the element iodine was not due to any other cause than its uniting with the constituents of the glass. Under

* A Paper presented before the St. Louis Academy of Science.

the influence of the electric discharge, iodine certainly acquires superior chemical affinities, attacking the substance of the glass, and forming iodides, and, from the disappearance of one-fifth of the volume of gas, I should say, also some iodates. To meet this eventuality, I resorted to sulphuretted hydrogen previous to precipitation.

The changed brilliancy of the spectral hydrogen lines that Mr. Smyth observed must, then, it seems to me, be attributed to another cause than a generation of hydrogen by a decomposition of iodine. First of all, it is certain that the changed condition of the tension in the tube has something to do with it.

I determined to decide the matter experimentally. An excess of iodine was sealed up in the same kind of tube that I used above. On passing the discharge at the ordinary temperature, only faint indications of hydrogen were observed in the spectroscopy. The tube was then heated gently, so that a great part of the iodine was volatilised. As the temperature rose, and the iodine vapour became more and more dense, to my surprise the hydrogen blazed in the spectrum with remarkable brilliancy. On cooling, the spectrum slowly changed back to its original appearance; hydrogen was again only faintly perceptible. It was clear then why the hydrogen lines in Mr. Smyth's tube should become so brilliant after the disappearance of the iodine. This latter is capable of binding hydriodic acid, which is the form in which the hydrogen is introduced into the tube. When by the process of action of the iodine on the walls of the glass tube it becomes united with alkalies, this hydrogen, finally, is liberated entirely, and, *instead of an iodine tube, we have a hydrogen tube developed.*

On taking a tube containing iodine in an atmosphere of hydrogen, I found that at first the hydrogen lines were very bright at ordinary temperatures. However, after a short time, and on continued passage of the spark, the lines became more and more faint, and finally scarcely perceptible. On then heating the tube, the hydrogen lines became very brilliant, and on cooling again disappeared almost entirely. On opening such a tube, dense fumes of hydriodic acid were emitted.

These experiments I think show conclusively: firstly, *the cause of disappearance of iodine in tubes on long-continued sparking*; and, secondly, *why the iodine lines are replaced by hydrogen lines during that process.*

I shall probably be in a position to make further communication on the sparking of iodine in the near future.

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St. Louis, U.S.A.

THE ACTION OF ACIDS ON LITMUS.

By J. E. MARSH.

THE nature of the change which blue litmus undergoes when treated with acids has not been very satisfactorily explained. The change from blue to red is supposed to be due to the freeing of a red-coloured acid from a blue-coloured alkaline salt. Whatever the cause may be, there are some phenomena in connection with the reaction which are not without interest.

It has been noticed by occasional observers that some acids, under certain conditions, do not affect blue litmus. These observations have not received any special notice, since they are not generally mentioned in modern standard works. From these observations, and others which I have made myself, it appears that in general an acid, to affect blue litmus, must be more or less dilute; in other words, water is necessary for the particular reaction, whatever it may be, which occurs when blue litmus becomes red.

Sir H. Davy, in his well-known investigation of chlorine, states that gaseous hydrochloric acid instantly reddens

the driest litmus-paper. On the other hand, Gore found that liquefied hydrochloric acid did not redden litmus. It is possible that Davy did not dry his gas as well as his litmus, for I have found that dry litmus-paper in hydrochloric acid, dried with phosphorus pentoxide, does not appreciably alter in colour for some time. Ordinary concentrated sulphuric acid does not redden litmus-paper, but imparts a more or less bluish purple tint to it; and the Nordhausen acid acts similarly. Pelouze, some fifty years ago, stated that acetic acid does not redden blue litmus. In fact, dry litmus-paper immersed in glacial acetic acid remains practically as blue as it was before. Propionic, butyric (normal and iso-), and valeric acids behave in precisely similar manner. On the other hand, fuming nitric acid and this acid, mixed with strong sulphuric acid, immediately redden litmus-paper. A striking lecture experiment consists in placing a piece of blue litmus-paper in distilled water, and another piece, after having been dried in a desiccator, in glacial acetic acid. The paper in the acid is then taken out and dropped into the water, when both the papers rapidly change from blue to red. Another experiment of even a more striking character, but less visible to a large audience, consists in writing with water on a piece of dried litmus-paper made from writing-paper. The superfluous water is removed by blotting-paper, leaving the writing perfectly invisible. On now plunging the paper into glacial acetic acid, the writing appears at once as a bright red on the blue ground of the rest of the paper.

These experiments serve to show that water is necessary for the action of acid on litmus. The apparent exception in the case of nitric acid is easily explained. Nitric acid is, of all ordinary acids, the one which most readily attacks organic matter, the action consisting in the introduction of the nitroxyl (NO_2) group, with elimination of water. Here, then, we have water liberated in the immediate neighbourhood of the colour, which is thus acted upon by a dilute acid.

THE APPLICATION OF DOUBLE PYROPHOSPHATES FOR THE ELECTROLYTIC SEPARATION AND DETERMINATION OF METALS.

By DR. ALBANO BRAND.

THE consistence of a metal reduced electrolytically is greatly dependent upon the state of combination in which it is present in the electrolyte. The double salts of organic acids, especially oxalic acid, are peculiarly suited for the production of good deposits, as well as for the quantitative separation of many metals.

The double pyrophosphates, as G. Vortmann has shown, behave with dilute acetic acid very much like the double oxalates. The double salt in solution is split up by the acid, and a crystalline, probably acid, salt separates out in the faintly acid liquid. This similar behaviour of the two series of salts, to which Prof. A. Classen has drawn attention, induced the author to study the electrolytic behaviour of the double pyrophosphates.

Hitherto only the double salts of nickel, tin, and gold have been applied in galvanoplastics. Concerning the electrolytic behaviour of the phosphates the only existing document is a paper by Thomas Moore (CHEMICAL NEWS, 1886, p. 209).

General Behaviour of the Double Pyrophosphates in the Formation of Electrolytes.

On the addition of an alkaline phosphate to a metallic salt dissolved in water, there is formed, with few exceptions, a phosphate insoluble in an excess of the precipitant. But if a neutral solution of a metallic salt is mixed with sodium or ammonium pyrophosphate, there is

formed a precipitate which is more or less soluble in an excess of the precipitant, forming a double pyrophosphate. The behaviour of acid sodium pyrophosphate is similar. A portion of a recently precipitated phosphate is also re-dissolved by a solution of alkaline pyrophosphate.

The solution of sodium pyrophosphate, and consequently the solution of the double salt, have a basic reaction. If the latter is submitted to electrolysis, and if the metal is deposited, pyrophosphoric acid is set free and the solution becomes acid, *i.e.*, it approximates to the initial condition of a solution prepared with the acid sodium pyrophosphate. Some metals separate from this acid solution as readily as from a neutral liquid; in others, the nature of the deposit is altered or the separation of the metal ceases, and can be renewed only on a corresponding re-inforcement of the current.

The application of the double pyrophosphates would, in consequence, be limited to the first-mentioned cases if the solution could not be kept neutral or basic. But this is practicable, as the solutions of the double salts (with few exceptions, which will be mentioned below) bear the addition of ammonia or ammonium carbonate to any extent without becoming precipitated. Soda-lye generally occasions precipitation.

In consequence of the possibility of keeping the electrolytes, neutral alkaline chlorides can be used as well as sulphates or nitrates. The metals reduced from a strongly alkaline solution, and from a pyrophosphate, are generally of an equally good condition.

The addition of ammonia or ammonium carbonate is further important, as it renders an excess of sodium pyrophosphate superfluous. If to a neutral saline solution there is added so much solution only of sodium pyrophosphate as is required for the formation of the pyrophosphate, the salt which has been separated dissolves on the addition of ammonium or ammonium carbonate in all cases where the solution, in an excess of the precipitant, supported the addition of these reagents without becoming precipitated.

The soluble double pyrophosphates bear also, without precipitation, the addition of ammonium oxalate—a behaviour which is of value in some cases.

Dilute acids precipitate probably acid pyrophosphates from the solutions of the pyrophosphates in an excess of the precipitant; these precipitates are now under examination. Some of them (*e.g.*, those of cadmium, manganese, zinc, cobalt, and iron [ferrous]) are completely insoluble in dilute acetic acid. If dilute mineral acids are employed the precipitate first formed is re-dissolved on the further addition of the acid. If the acid is first neutralised with ammonia or ammonium carbonate the precipitate re-appears, but dissolves again on a further addition of the reagent. It is to be assumed that a double ammonium salt is here formed. The same appearance is repeated if the solution of the alkaline pyrophosphate is added to a saline solution with an excess of acid so that no precipitation of a double salt takes place. By reason of this behaviour we may prepare a solution of a double salt suitable for electrolysis by setting out from an acid solution.

This behaviour of an acid salt, *i.e.*, solubility in an excess of an alkaline pyrophosphate, and bearing the addition of ammonia or ammonium carbonate without precipitation, has been, for the sake of brevity, designated in the following memoir as *normal*.

Sodium pyrophosphate is relatively sparingly soluble. A solution saturated at 18° contains in 10 c.c. about 1 grm. of the salt ($\text{Na}_4\text{P}_2\text{O}_7 + 10\text{H}_2\text{O}$). Ammonium pyrophosphate is considerably more soluble, since 1 c.c. of water takes 1 grm. of the salt. There is scarcely any advantage to be recognised in the use of the latter, and as it is about ten times as costly as the former on account of the difficulty of its preparation, and as it is not regularly crystallised, the use of the sodium salt is to be recommended.

As some of the double salts are deposited on heating it

is advisable to keep solutions of sodium pyrophosphate ammonium carbonate, and ammonium oxalate in store.

The alkaline pyrophosphate is not affected by the electric current; at least, the author has not been able to observe any change.

Behaviour of Metals on the Electrolysis of their Double Pyrophosphates.

1. *Nickel*.—The behaviour of the nickel salts in the preparation of the electrolyte is in all respects normal. The whitish green precipitate of the pyrophosphate readily dissolves in an excess of the precipitant with a yellowish green colour, which turns green on the addition of ammonium carbonate and blue if ammonia is added.

Nickel is deposited from pyrophosphoric or alkaline solution as a greyish-white metal of excellent quality, compact, and adhering closely to the cathode. In a pyrophosphoric solution a powerful current is needed, especially towards the end of the process, and the deposit must be washed without interrupting the current. Of the alkaline solutions, that mixed with ammonium carbonate is preferable to one to which free ammonia has been added.

In a solution containing ammonium carbonate great latitude is permissible as regards the strength of the current. The deposition begins with currents yielding less than 0.1 c.c. of detonating gas per minute. With a current of 2–3 c.c., from 0.2 to 0.3 grm. of nickel can be quantitatively deposited in twenty-four hours. But the same quantity, and equally good in quality, can be deposited in a few hours with a current giving off 20 c.c. and upwards of detonating gas per minute. The reduction can be further accelerated by the application of heat.

The end of the decomposition may be recognised when no darkening is produced in a few c.c. of the electrolyte on the addition of pale ammonium sulphide.

The treatment of the metal at the close of the reduction, in ordinary cases, is that commonly followed. The liquid is poured off, the deposit is rapidly washed with distilled water, and then rinsed with absolute alcohol; the tared capsule is then dried at about 100°, let cool in the exsiccator, and weighed. If the current is very feeble, and if the solution has been mixed with ammonium carbonate, there is formed on the anode a slight brown deposit, which disappears spontaneously if the current is interrupted for a short time. In one instance its weight after drying is 0.0016 grm. This does not occur in ammoniacal solutions.

2. *Cobalt*.—Cobaltous pyrophosphate is pale red, and dissolves with a violet colour in an excess of the precipitant. The addition of ammonium carbonate does not affect the colour, but ammonia turns it first brown and then violet. On the electrolysis of its double pyrophosphates, cobalt behaves similarly to nickel, and separates out with its peculiar brownish colour. In other respects it behaves like iron, as the metal is slightly dissolved by the electrolyte. For the precipitation of the last traces a current of 10–15 c.c. is necessary, and it must be washed without interruption of the current. The brown colour, which traces of the metal give with ammonium sulphide, is more intense than that of nickel, and consequently the end of the reaction is more distinctly perceptible.

3. *Iron*.—In the preparation of the electrolyte ferric salts behave normally. Ferric pyrophosphate is white, and gives with an excess of sodium pyrophosphate an almost colourless solution. On the addition of ammonia it becomes yellowish brown to brown-red, according to the degree of concentration.

Ferrous salts also behave normally; they give a white precipitate, and in an excess of the precipitant a light green solution. On the addition of ammonia the solution becomes darker as the iron is peroxidised. If the colour becomes a red-brown there begins the separation of a basic salt of the colour of ferric hydroxide.

For electrolysis, in which iron behaves like nickel and cobalt, the solution mixed with ammonium carbonate is alone suitable. If the ammoniacal solution of the ferric double salt or that of the ferrous salt recently prepared is submitted to electrolysis there is deposited at the anode at first a reddish brown salt, which is strongly adhesive and which contains ferric oxide and pyrophosphoric acid. Metallic iron is deposited at the same time at the cathode. As long as the coating on the capsule is thin the colour of the reduced iron is a slate-blue; afterwards it appears iron-grey.

The reduction of iron begins with feeble currents, but for its rapid separation a current of 20 to 30 c.c. of detonating gas per minute is required. It is especially difficult to eliminate the last traces, so that if large quantities of iron have to be precipitated the decomposition may be conveniently begun with the current of two Bunsen elements connected in series, and towards the end the enfeebled current is reinforced by the introduction of a third element.

After completion of the reduction it is necessary to wash without interrupting the current, as the electrolyte has a distinctly solvent action upon the deposited metal. This is the reason why the reduction of the last traces is so difficult.

4. *Manganese*.—Manganous salts yield with sodium pyrophosphate a white precipitate which re-dissolves in a large excess of the precipitant. In ammonia the precipitate is very easily soluble; it dissolves also in ammonium carbonate, but a white salt here soon separates out. The double ammonium salt behaves like the sodium salt. On the application of heat precipitates appear which do not disappear on cooling.

The double pyrophosphates of those metals which form peroxides behave electrolytically different from the salts hitherto examined.

If we electrolyse the solution of a manganous salt in an excess of sodium pyrophosphate, we obtain, with currents of about 20 c.c. detonating gas per minute, a brown solution, but no manganese peroxide is separated. The solution (remaining at first clear) contains a double salt in which the manganese exists in a higher state of oxidation. Subsequently, especially if much manganese is present, there appears a brown flocculent precipitate of manganic hydroxide. With a weaker current (10 c.c. detonating gas per minute) some manganese peroxide is separated and adheres firmly to the anode. If the strength of the current decreases this separation of peroxide predominates, though the formation of the brown solution does not cease. At the cathode is seen, more or less, according to the strength of the solution, the characteristic colour of permanganic acid.

(To be continued).

ELECTRICITY IN CHEMICAL MANIPULATIONS.

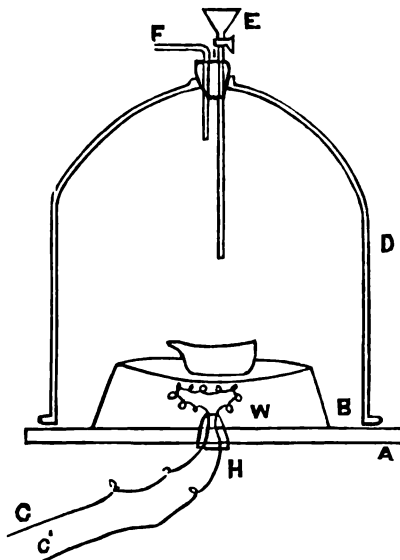
By REGINALD FESSENDEN,
Chemist, Edison Laboratory, Orange, New Jersey.

A DESCRIPTION of a few pieces of chemical apparatus in which electricity is employed may be of interest.

The current is derived from a simple primary battery, described below.

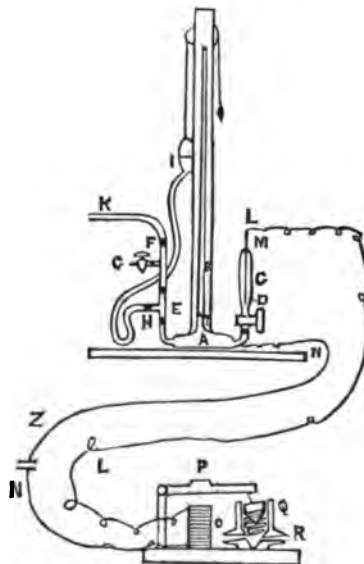
1. *For Rapid Evaporation in Vacuum*.—A, is a piece of plate-glass, through the centre of which a hole is bored by means of a brass tube and emery; in the hole a cork, H, is inserted, and two wires, G G, run through it, each connected to one end of the platinum loop, W, which latter is packed with magnesia or any such material. The operation is as follows:—The dish, C, containing the substance to be evaporated, is placed on the stand, B, and the bell-jar placed over all. The tube, F, is connected to the filter-pump, and the wires, G G, to the terminals of the battery. Evaporation proceeds with extreme rapidity.

More liquid is added from time to time through the separatory funnel, E. Where the current is obtainable,



electric incandescent lamps may be used, in place of wire, with advantage.

2. *Automatic Heat Regulator and Air Thermometer*.—A is a piece of glass tube, 4 inches long and 1 inch in diameter, having three nipples, one connected to a piece of thermometer tubing, B, one to a short piece of tubing, C, drawn out very fine at D, and having a cock at its lower extremity, and the third to the T-piece, E. K is a tube connecting with the air bulb, which may be of Bohemian glass; I is a bottle of mercury, connecting by a rubber



tube with H; N is a platinum wire, fused into A; M is a thin carbon rod, resting on the capillary portion of C, and connected to the wire, L. There are cocks at H and T. Q is an electro-magnet, connected to the wires L and M; Q is a plunger, held up by a spring in a piston, so that the gas can pass freely through the opening, R, to the

burners so long as the magnet is not acting. The operation is as follows:—Cocks H and T open, cocks G and D shut; it is a simple air thermometer, readings being taken on the tube D. To use it as a regulator, the bath is raised to the required temperature, cocks G and D are opened, and the mercury adjusted so that it nearly touches the carbon rod, M; cocks G, H, and T are then closed. It will be seen that if the temperature rises ever so slightly the mercury will touch M, and the current from the battery, Z, flowing through the wires L and N, will pull down the armature, P, driving the cylinder, Q, down, and shutting off the gas, except so much as may be necessary to keep the burners lighted.

This apparatus will maintain the temperature constant for days to half a degree; hence it is of use in accurate and long fractional distillations. It works with any kind or pressure of gas, and one cell will keep it going for months.

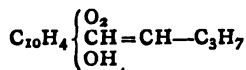
(To be continued).

ON THE CONSTITUTION OF LAPACHIC ACID AND ITS DERIVATIVES.*

By SAMUEL C. HOOKER and WILLIAM H. GREENE.

In 1857, Arnoudon† described, under the name Taiguic Acid, a yellow colouring matter existing in the Taigu wood of Paraguay; nine years later, Stein‡ described as greenhartin a similar matter which he had extracted from the greenheart of Surinam. In 1879, Paterno§ proved the identity of these substances with the lapachic acid obtained by Siewert from the Lapacho tree of South America. Finally, we have recently found the same substance in a South African wood, the Bethabarra.||

Paterno,¶ in an admirable research published in the *Gazzetta*, 1882, has assigned to lapachic acid, with a very great degree of probability, the following constitutional formula:—



Oxy-amylenaphthaquinone.

The results from which this formula is mainly deduced are the following:—

Lapachic acid gives a series of stable salts, but all experiments failed to reveal the true acid group, COOH.

On distillation with zinc dust, naphthalene and isobutylene were obtained.

On oxidation with nitric acid, phthalic acid was formed.

By reducing agents, a hydrolapachic acid was obtained, which rapidly absorbed oxygen, becoming re-converted into lapachic acid.

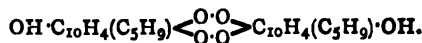
A monacetyl derivative was obtained.

Hydriodic acid and phosphorus gave a liquid hydrocarbon, which was taken to be amylnaphthalene.

In the course of the study of this acid, Paterno prepared several compounds, which he was only able to explain satisfactorily by the assumption that two molecules of the acid had taken part in the formation of each of their molecules.

By the action of concentrated sulphuric acid on lapachic acid, a compound crystallising in beautiful red needles is formed, which has precisely the same percentage composition as lapachic acid. This compound, which is known

as lapachone, was assigned the following formula by Paterno:—



Lapachone is insoluble in alkaline carbonates; it is soluble in caustic alkalies only after boiling for some time. According to Paterno it separates from the alkaline solution on cooling, and is almost completely precipitated unchanged on the addition of acids.

While recently engaged on the study of the colouring matter of Bethabarra wood, subsequently proved by us to be lapachic acid, we obtained an orange-red quinone-like substance. In the course of our experiments with this compound we observed a number of reactions which, when we had afterwards identified the compound as lapachone, did not agree with Paterno's view of its constitution.

We found that lapachone shows many of the characteristics of a chinone. It gives a white crystalline compound with acid sodic sulphite, which is re-converted by acids and alkalies into the original substance. It forms compounds with hydroxylamine and ammonia with great readiness, and gives the quinone colour reaction of Bamberger.

These reactions are obviously not reconcilable with the formula given above, and point to the probability that lapachone is $\text{C}_{15}\text{H}_{14}\text{O}_8$, and not $\text{C}_{30}\text{H}_{28}\text{O}_6$.

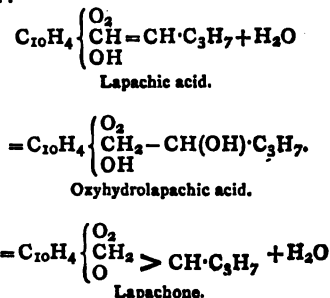
A determination of the molecular weight of lapachone, by Raoult's method, gave figures confirming this supposition, thus proving that only one molecule of lapachic acid is concerned in its formation, a result borne out by other facts.

Calculated for Paterno's formula $\text{C}_{30}\text{H}_{28}\text{O}_6$.	Calculated for $\text{C}_{15}\text{H}_{14}\text{O}_8$.	Found.
484	242	255

It remains, therefore, to explain how a substance having such strong acid tendencies as lapachic acid, dissolving with ease in alkaline carbonates, can be converted into an indifferent compound like lapachone, and yet retain the same percentage composition.

Although Paterno's formula of lapachic acid cannot be considered in any way proved, it lends itself well to the explanation of the formation of lapachone, and in this way considerable indirect proof is furnished of the probable correctness of Paterno's views in regard to lapachic acid.

It seems lawful to assume that under the influence of strong mineral acids (concentrated nitric acid in the cold acts similarly to concentrated sulphuric acid as shown by Paterno) lapachic acid takes up a molecule of water, giving rise to an intermediate compound, which is at once decomposed by the acid, again splitting off water, but in a different direction. This is shown in the following equation:—



The fact that phthalic acid is produced by the oxidation of lapachic acid would appear to furnish proof that all the side groups are situated in the same benzene nucleus, and consequently whether lapachic acid be a derivative of α or β naphthaquinone the (OH) group must be in the ortho

* Read at the Chemical Section of the Franklin Institute, May 27, 1889.

† *Comptes Rendus*, xli., 1152.

‡ *Journ. Prakt. Chemie*, xcii.

§ *Gaz. Chim. Ital.*, ix., 506.

|| *American Chem. Journal*, xi., 26

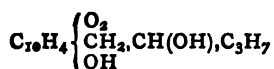
¶ *Gaz. Chim. Ital.*, xli., 337—392.

position to the amylene chain: this favours the probability of the occurrence of the above condensation.*

This view of the constitution of lapachone, *i.e.*, regarding it as a derivative of naphthofurfuran, agrees very thoroughly with all its properties and reactions so far observed. It has, moreover, received direct confirmation from the result of an experiment which was made to obtain, if possible, corroboration of our views.

Paterno states, as already mentioned, that lapachone is insoluble in caustic alkalis in the cold, but dissolves on heating, and is, in part, deposited from the filtered solution unchanged as it cools.

This observation seemed at variance with our idea of the constitution of lapachone, and we consequently carefully repeated Paterno's experiment. The insolubility of lapachone in alkaline carbonates and caustic alkalis in the cold is readily explained by the constitution we have assigned to it, and its solubility on boiling is best accounted for by the supposition that the furfuran ring is split by the action of potash, that one molecule of water is taken up with the formation of a salt of the compound—



Oxyhydrulapachic acid.

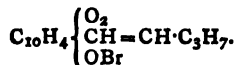
which we had previously supposed to exist as an intermediate product in the formation of lapachone. This explanation proved quite satisfactory, for on neutralising with acetic acid, a red oil was obtained which, in the course of an hour or so, solidified to a yellow crystalline mass.

Analysis proved it to have the expected composition. The tendency of the new substance to pass into lapachone under the influence of dilute mineral acids is very great, and hence if dilute HCl acid be used for the precipitation, either a mixture of lapachone and the new compound or lapachone only is obtained.

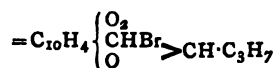
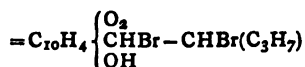
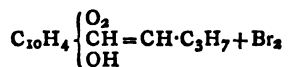
We have not yet succeeded in preparing the potassium salt of the new substance in a crystalline form, but as its barium salt, which crystallises very readily in bright orange needles, closely resembles lapachone, it is not improbable that the potassium salt may have a similar appearance, which would account for Paterno's supposition that the crystals deposited on cooling and before the addition of hydrochloric acid were crystals of lapachone. It is right to add that the fusing-point of these crystals was found by Paterno to be almost identical with that of lapachone.

The salts of the new compound, as might be expected, dissolve to the same intense red colour as those of lapachic acid. It melts at 125°, and is very readily soluble in most ordinary solvents. It may be obtained in comparatively large crystals by spontaneous evaporation of its solution in alcohol or acetic acid.

By the action of bromine on lapachic acid in acetic acid solution, Paterno obtained a compound which he regarded as monobrom-lapachic acid, and to which he assigned the formula—



Considering the properties of this compound and the probable constitution of lapachic acid, its formation would seem to be better explained by the supposition that an addition product is first formed, and that this, by splitting off hydrobromic acid, gives rise to the formation, not of brom-lapachic acid, but of brom-lapachone, thus—



We are at present endeavouring to prove the truth of this supposition, and have already observed some important facts tending to show the correctness of our views.

The formation of several of the other compounds obtained by Paterno would appear to be better explained in a similar manner to the foregoing than by the formulæ he has assigned to them. We prefer, however, to leave the discussion of these until our work has progressed further. In the meantime, we wish to say that, although we are hopeful further experiments will justify our present conclusions, we do not regard them as of necessity final, and have only been induced to make this preliminary communication to ensure to ourselves the undisturbed continuation of the work, which, owing to many causes, can not, unfortunately, proceed with as great rapidity as we could desire.

ON LAPACHIC ACID AND ITS DERIVATIVES.*

By E. PATERNO.

In the *American Chemical Journal*, April, 1889, p. 267 I have read an important note by W. H. Greene and S. C. Hooker, in which is proved the identity of the colouring-matter of Bethabarra wood with lapachic acid. In ending their note the authors propose to study lapachone, and suggest that certain reactions observed by them lead to the belief that this compound has not the constitution provisionally assigned by me in 1882.†

I must draw the attention of these two chemists to the fact that in my memoir, after having stated that the constitution of lapachone was perhaps the most difficult and important point to determine, I terminated by saying that all my considerations had a very limited value, and I dwelt on it but a moment, with the sole design of showing the importance and the range of the argument of which I had undertaken the study.

It is indeed true that since 1882 I have published nothing on lapachic acid. I have been occupied with other matters, it has been difficult for me to obtain first materials, and I did not desire to publish the results in parts, especially when I had reserved the right of continuing the research. However, that I have never abandoned the work is shown by the fact that in my research on Raoult's law, published conjointly with Nasini in 1886,‡ we proved that lapachone is not a polymeric derivative of lapachone, as I at first supposed, but that it corresponds to the simple formula $\text{C}_{15}\text{H}_{14}\text{O}_3$, and I said that while the polymeric quinones so far studied are brown substances, only slightly soluble, and having fusing-points much higher than the corresponding quinones, these great differences in external characters are not observed between lapachic acid and lapachone. Since that time, as I have besides announced a few months ago,§ I have continued this research with greater industry, and, by applying Raoult's method I have shown that the acetyl derivative of lapachic acid fuses at 131–132°, for which I had ad-

* It is, of course, possible, though scarcely probable, that lapachic acid is derived from $\beta\beta$ -naphthaquinone, in which case the relative positions of the amylene chain and the hydroxyl group would be the para.

* Read at the Chemical Section of the Franklin Institute, June 18, 1889.

† *Gazzett. Chimica*, xii., 337.

‡ *Ibid.*, xvi., 262.

§ *Ibid.*, xix., 3.

vanced a complex formula, corresponds rather to that of a diacetic derivative of lapachic acid or of lapachone, or more probably another isomeride of this substance; and in a series of researches that I may say are complete, and which were in part made together with Sig. Minimi, I have entirely re-considered the study of those derivatives of lapachic acid of whose constitution I entertained doubts, and, in particular, lapachone, the diacetyl derivative and the magnificent substance crystallising in splendid bronze-red laminæ. Of lapachic acid and lapachone we have studied the oxime and hydrazin compounds, we have obtained the quinone corresponding to the diacetyl derivative, we have prepared and studied the triacetyl derivative, corresponding to the reduction derivative of lapachic acid, the compound of lapachic acid with thiophen has been prepared, and in this manner we have collected together a considerable number of facts which completely elucidate the constitution of lapachone and many other derivatives of lapachic acid.

I am sure that Messrs. Greene and Hooker will, after what I have exposed, allow us time to publish our labours, and desist from the further investigation of lapachic acid derivatives, at least until after the publication of our researches.

A DESCRIPTION OF SEVERAL YTTRIA AND THORIA MINERALS FROM LLANO COUNTY, TEXAS.*

By W. E. HIDDEN and J. B. MACKINTOSH.

History.—In July, 1886, the first piece of gadolinite (a mass of about 1½ lbs.) was accidentally discovered, by Mr. J. J. Barringer, in Llano County, Texas. It was noticed projecting from an outcropping of granite, and was detached therefrom and preserved merely because of its peculiar appearance. Later, Mr. Barringer commenced digging at the locality, and in a short time he unearthed a pocket of huge crystals and masses of this rare mineral aggregating not less than 500 kilos. This remarkable quantity was obtained by digging with pick and shovel, in the partly decomposed surface rock, and all came from a space not over 4 ft. deep, 3 ft. wide, and 8 ft. long.

Until August, 1888, the true nature of the mineral remained unknown, and meanwhile it received such local names as "tin-ore," "black-jack zinc," "volcanic glass," &c. Later the name "samaraskite" was given to it, and as such it was known until Mr. Barringer, upon sending it to New York in an endeavour to find a market for it, received the information that it was gadolinite. About this time it came under the notice of one of us, and an effort was made to develop the locality thoroughly. Thus far, only the gadolinite had been found, and no value having been attached to it, the mineral had been free to all who desired "a few pounds of it." Of the large quantity obtained in 1886, only about 100 kilos. then remained, the greater portion having been gradually distributed among local visitors. In January of this year, realising that a locality that could produce the rare mineral gadolinite in such unprecedented masses as had already come under our notice was worthy of careful investigation, we sent Mr. Wm. Niven, of New York, on a special visit to the region, and it was the series of specimens collected by him that induced one of us to personally visit the locality. This was done during the past summer, two months being spent in prospecting the whole region; the results of this investigation are embodied in this announcement.

Description of Locality.—The spot where the gadolinite has been found is nearly five miles southward from Bluffton, in Llano Co., Texas, and on the west bank of

the Colorado River. The whole surrounding region for many miles is Archæan* (with occasional cappings of limestone), and granite, in various shades of colour and texture, is the common country rock. A coarse textured deep red granite is most abundant, and through it numerous and extensive quartz veins extend to the surface. Only in these veins have the ores of yttria, &c., been found, and only in the wider swellings of these veins or where they have assumed the character of bold uplifts, have masses of large size been found. Here is to be seen a mound-like elevation, 100 × 150 feet in area, projecting boldly from the surrounding granite, and 27 feet in elevation above the river terrace. It is made up of huge blocks and masses of quartz and red felspar, all tightly massed together. The mound is nearly circular in form, and the contact with the country granite is sharply defined. It is plainly seen to be a widening of a vein that can be traced in a south-westerly direction for some distance and one of a series to be seen at several locations in the near neighbourhood.

The quartz masses are from 5 to 20 feet thick, with the interstices filled completely with a highly crystalline red felspar. Between these irregular masses are found at times thin seams of a black iron-mica, and with this mica, and in the adjacent felspar, are found the various ores of the rare earths hereinafter to be noticed.

From all sides this mound has been entered with trenches, and one or more of the yttria minerals have been found at every opening. At this writing it has been so much cut into by trenching that it is difficult to trace the original boundary. On the river side the mound is rather steep, but in other directions its sides slope gradually. Its top is flat and consists of pure white quartz (bleached by weathering), and it is only on the slopes and at the base that the several rare minerals show themselves. The quartz and felspar are very much stained with red oxide of iron and some yellow and green uranium compounds at the points where at present the larger mineral masses have been found, and these stains have constituted a good guide to their discovery.

Up to the present time we have identified the following mineral species, but we will describe in detail only the more important in the present paper. The list of species includes quartz, hyalite, orthoclase, albite, biotite, muscovite, magnetite, martite, gadolinite (several varieties due to alteration), fergusonite (three varieties of hydrous species), allanite, molybdenite, molybdate, cyrtolite (several varieties), fluorite, gummite (two varieties), a carbonate of the rare earths (tengerite?), a thorium-yttrium-lead uranate, a hydrous uranium thoro-silicate, an yttrium-thorium silicate, a fetid gaseous compound (which we first observed upon breaking some of the material for analysis), and several minerals, found in small quantities, which we have not had the opportunity to identify with certainty.

Quartz is rarely found crystallised at this locality. Only one pocket of smoky crystals (coated with ferric oxide), of noteworthy size and transparency, having been as yet found. Small druses of quartz-caps are often met with in the seams of the larger quartz masses.

Hyalite, in mammillary forms, was observed coating the seams of the felspar and quartz, in very small patches.

Orthoclase occurs massive and finely crystallised and in great variety of form. Twin crystals, of curious complexity, and simple forms are very common. Crystals of huge dimensions, a foot or more in length, more or less perfect, and smaller sizes, abound; especially are they abundant on the contact of the vein with the granitic walling.

Albite is rare, and occurs coating small cavities in the massive orthoclase. Crystals not above 1 inch diameter were observed.

* From the *American Journal of Science*, Third Series, vol. xxviii., No. 228, December, 1889.

* See "Geologic Story of the Colorado River," R. T. Hill, in *American Geologist*, vol. lili. No. 5, pp. 291-2.

Biotite (?) is very abundant, and occurs in broad folia in the seams between the quartz and felspar masses. Diagonal prismatic cleavage surfaces were common. It was intimately mixed with much magnetite, and was often the matrix or foundation upon which the rarer minerals rested. Many alteration products were noticed.

Muscovite is quite rare, and occurs as hexagonal implanted prisms only in the albitic cavities. These prisms seem to be made up of 3 or 6 sectors on a basal section. No examination, chemical or optical, has been made.

Magnetite is quite abundant, both massive and crystallized. It is always associated and intermixed with the biotite. Octahedral crystals with planes of the cube, rhombic-dodecahedron and of a trapezohedron were found abundantly, though superficially they were coated with a thin micaceous layer and some uranium hydrate.

Martite was very common, being an alteration from the magnetite. Crystals having a black colour interiorly and preserving the cleavages of magnetite, but having no magnetic properties, were very commonly observed.

Gadolinite.—We have already detailed the events surrounding the discovery of this mineral in Texas. For a description we would refer to the paper by Dr. Genth,* in the *American Journal of Science*, September, 1889. As Dr. Genth as stated, this gadolinite, when unaltered "has a black colour; in thin splinters it is translucent with a dark bottle-green colour; the fine powder is greenish grey; fracture conchoidal to splintery. Specific gravity 4.201—4.254."†

Most of the gadolinite is altered into a brownish red mineral of waxy lustre; some of the masses are entirely so altered, while in others the change has only taken place superficially. A further alteration has been to a yellowish brown earthy (ochreous) substance, which upon drying in the open air becomes a very light powder. The average size of the masses of this Texas gadolinite has been, in our experience, about half a pound; though embedded crystals (hydrated) were noticed not above half an inch long by one-quarter inch wide (very acutely terminated), and as to large masses there were many of 5, 10, and 15 lbs. each. One double crystal weighed forty-two pounds, and was nearly free from matrix. Another huge pointed mass, in reality a crystal, weighed fully sixty pounds.‡ All of the gadolinite had, at some time in the past, presented smooth crystal surfaces (as the hydrated crust often gave evidence of), but very few masses were found without more or less exterior alteration. This alteration had roughened the underlying surface and had given a dark brick-red colour to all the changed mineral.

On only three crystals were we enabled to find sufficiently smooth surfaces to give us even approximate angles, and these we here append:—

$I \wedge I = 115^\circ - 117\frac{1}{2}^\circ$	$O \wedge \frac{1}{2}I = 145^\circ - 146^\circ$
$I, I = 156^\circ - 158\frac{1}{2}^\circ$	$\frac{1}{2}I, \frac{1}{2}I$ (ov. O) = $111^\circ - 112^\circ$
$I, I = 119^\circ - 119\frac{1}{2}^\circ$	$O, I = 90^\circ - 91^\circ$
$I, O = 113^\circ - 113\frac{1}{2}^\circ$	I, I (ov. $\frac{1}{2}I$) = $77^\circ - 79^\circ$
$-I, +I$ (ov. O) = 46°	$\frac{1}{2}I, I = 123^\circ - 126^\circ$

All the crystals observed were lengthened in the direction of the vertical axis (in one instance, ten inches long), and the plus and minus 1 and 2 pyramids are present often to the total extinction of the basal pinacoid, making acute forms difficult to extract from the matrix in perfect condition. A distinctly monoclinic habit was apparent in many of the masses, and the pyramid 2 was often developed only upon the plus or minus side. The basa,

plane was only noticed in one instance. At another vein, one mile south, two crystals of gadolinite, of rare beauty and perfection, were found on the land of Mr. Hiram Casner; this goes to show that other discoveries of the rare minerals are possible in the neighbourhood.

YTTRIALITE, a new Thorium-Yttrium Silicate.

The mineral, which we have named Yttrialite, was discovered associated with, and often upon, the gadolinite, and but for its characteristic orange-yellow surface alteration (that of gadolinite immediately alongside of it being invariably of a dull brick-red colour) it might have continued to pass for "green gadolinite," which was the local name given to it. Of these yellow masses, one weighed over ten pounds, and twenty kilos. were found in all. Upon being broken open they are of an olive-green colour tending in places to a drab shade. Peculiar minute ragged lines permeate the mineral in all directions, causing an apparent muddiness or semi-opacity. No crystals have as yet been observed, but a seemingly orthorhombic symmetry was apparent in some of the masses. The mineral breaks easily in two directions, with a shell-like fracture, but separates into small flakes very readily. (Gadolinite is broken only with difficulty). Nothing like a cleavage has been noticed. A thin white crust of a mineral related to tengerite occupies the cracks in the mineral, and this is equally true concerning the gadolinite of the locality, as Genth has already noted. We have named the mineral *yttrialite*, in allusion to the prominent part played by the yttria earths in its composition.

The specific gravity is 4.575; hardness 5—5.5. It is readily soluble in hydrochloric acid. When heated over the Bunsen flame it decrepitates violently, and falls to powder upon being ignited over a blast, becoming snuff-brown, infusible, and insoluble. These characteristics serve to at once distinguish it from gadolinite, which has specific gravity from 4.2 to 4.3 (Texas varieties), and which when heated glows vividly and swells into ragged fragments. The analysis shows several fractions of the yttria earths (A, B, C, D), which were separated by successive precipitations with sodium sulphate. The atomic weight of each fraction was determined, showing successive increase with each separation. The fractionation was discontinued after the fourth separation, as the amount of material was getting very small, but the atomic weight shows that the lanthanum and didymium are still mixed with an earth of higher atomic weight. The results obtained are as follows:—

	Per cent.	Oxygen ratio.
SiO ₂	29.17	97.234 = 4
PbO	0.854	0.383
ThO ₂	12.00	9.108
MnO	0.77	1.084
FeO	2.89	4.014
CaO	0.60	1.071
Al ₂ O ₃	0.55	1.617
Ce ₂ O ₃	1.86	1.722
Atomic weight.		72.918 = 3
(A) Y ₂ O ₃	22.67 = 110.3	25.320
(B) Y ₂ O ₃	5.30 = 110.53	5.910
(C) Y ₂ O ₃	4.50 = 114.9	4.860
(D) Y ₂ O ₃	14.03 = 120.	14.616
(LaDi)O ₃ , &c. ..	2.94 = 162.	2.370
UO ₃	0.83	0.843
Ignition loss ..	0.79	
99.754		

Total yttria earths = 46.50 p.c. Erbium spectrum distinct.

Regarding the loss by ignition as non-essential, the oxygen ratio of all the bases to silica is exactly 3:4, which leads to the formula R₂O₃, 2SiO₂, in which R₂O₃ may be replaced by its equivalent in RO, RO₂, or RO₃.

* Bakins found sp. gr. = 4.239; our own determination, on a very compact mass, gave us 4.306.

† Dr. Genth was misinformed by the party who supplied him with his "Burnet Co. gadolinite," as it has not as yet been discovered in that county, and the error of crediting Burnet Co. with having produced it was probably owing to the fact that it had been shipped from Burnet (Burnet Co.), which was the nearest R.R. point to the true locality some 19 miles distant.

‡ Stated on the authority of Mr. Barringer and many of his neighbours.

		Gadolinite, Llano Co., Texas.			
		GENTH.	Sp. gr. = 4.254. Oxygen ratio.	EAKINS.	Sp. gr. = 4.239.* Oxygen ratio.
SiO ₂		22.80	76.00	23.79	79.30
ThO ₂		—		0.58	
MnO		0.18		trace	
FeO		12.93		12.42	
GlO		9.19		11.33	
CaO		0.71		0.74	
MgO		0.11		traces	
K ₂ O		0.12			
Na ₂ O		0.23			
Al ₂ O ₃		0.31			
Fe ₂ O ₃		—	116.11	0.96	56.94
Ce ₂ O ₃		2.66		2.62	
(DiLa) ₂ O ₃		5.01		5.22	
(Y,Er) ₂ O ₃		44.45		41.55	
H ₂ O		0.79		1.03	
P ₂ O ₅		—	59.25	0.05	1.80
Insoluble		0.93		—	
		100.42		100.29	

There is no simple ratio between the sesquioxide and other bases. This mineral, therefore, differs from gadolinite in containing twice as much silica. It has other points of difference, viz., it contains no glucina, which has been regarded as a characteristic constituent of gadolinite, and there is a very large preponderance of sesquioxides among the bases. For comparison we append two analyses of gadolinite from this locality by Genth (*American Journal of Science*, September, 1889) and Eakins (private communication from Professor F. W. Clarke).

Regarding the water and phosphoric acid as accidental, and using the molecular weight for the yttria earths determined by Eakins (260) for the calculation of Genth's analysis, we get the oxygen ratio of all the bases to silica of 3.055 : 2 and 3.054 : 2 respectively, giving the general formula R_2O_3, SiO_2 , in which R_2O_3 may be replaced by its equivalent in RO and RO₂. Both of these analyses seem to show a tendency towards an equality of the sesquioxides to the monoxides, though there is a preponderance of sesquioxides in the one and of protoxides in the other. They differ also from our analysis of yttrilite in the small percentage of thoria, which in the latter amounts to one-eighth of the total bases in equivalency.

(To be continued).

NOTICES OF BOOKS.

The Story of Chemistry. By HAROLD W. PICTON, B.Sc. With a Preface by Sir HENRY ROSCOE, D.C.L., LL.D., F.R.S. London: W. Isbister (Limited).

THIS little book is truly, as Sir Henry Roscoe characterises it, "a short and attractive history of chemistry." It is not a series of biographical notices of the men who have made the principal discoveries in our science, but a view of the development of its leading ideas.

Mr. PICTON fully recognises the truth that chemistry did not originate in alchemy, but had a previous independent existence.

He accepts Pliny's somewhat mythological account of the accidental discovery of glass, and, what is much more strange, the story of Cleopatra dissolving pearls in weak vinegar. If we remember rightly, G. H. Lewes showed

that pearls are not, at least in any admissible time, soluble in vinegar.

The remarks on the construction and use of hypotheses are truly philosophical and should be had in remembrance by the student.

Roger Bacon is here admirably appreciated. This old-time thinker, as far back as the thirteenth century, perceived that force is invariably subject to mathematical laws. This is the more significant since, as the author reminds us, "even the great Kepler thought the revolutions of the planets might be accounted for by guiding spirits."

Mr. PICTON, it will be perceived, though a chemist, is not solely or exclusively one. Sometimes he raises questions which may make our modern industrialists thoughtful. For instance, we read here:—"Perhaps it may be well, therefore, to remind ourselves that the mere production of sulphuric acid, even to the amount of inland seas, is in itself no special boon. Chemistry has, so far, been applied to manufacture: good, but how far has the manufacture increased the happiness of life?"

Rudolf Glauber is quoted as denouncing "this mischievous composition and diabolical abuse of gunpowder." What would he have said could he have witnessed the development and use, or abuse, of the "high explosives"? With reference to the passage just quoted, our author says:—"What a man visibly *does* may not be so important as what he *is*. As Emerson puts it, 'we do not want actions, but men.' Here he comes in collision with Buckle, who tells us that what a man *is*, is overlooked, or is, at best, soon forgotten, unless his actions are such as to have earned the gratitude of the world."

The beginnings of science, in the present sense of the word, our author places in the seventeenth century. He does not, however, mention that alchemy did not even die with Woulfe in the beginning of the present century. Quite in our own day, a person unknown advertised in the *Athenaeum* his readiness to teach the "Hermetic Art" for a fee of 100 guineas.

Passing over the epochs of Boyle, of Mayow, Hales, and Black, we come to Phlogiston and its author, Stahl. The history of this aberration being, perhaps, equivalent in chemistry to that wrought in biology by the school of Cuvier, is ably and impartially given. It may, perhaps, be hinted that the ghost of phlogiston—"caloric"—is even yet not thoroughly exorcised, especially in France.

Priestley receives here something more than justice. We must remember that he was persecuted, not as a chemist and physicist, but as a reputed heretic and revolutionist. Had he followed the wise advice of Edward Gibbon, to stick to physical science and leave controversial theology

* At 17° C.

† Didymium spectrum very strong.

‡ Molecular weight = 260.

§ Erbium spectrum weak.

and politics alone, he would not only have lived and died in honour, but have acquired still stronger claims on our gratitude. In the account of Priestley's life, we find a slight error. Needham Market, his first residence after leaving Daventry, is not in Surrey, but in Suffolk.

The author does not point out Priestley's great defect—his versatility. That a man who dabbled in so many subjects should have done good service in any sphere is something remarkable.

The discoveries of Cavendish in electricity are not here noted; strictly speaking, they do not belong to the subject; but the fact that he could leave such sterling work unpublished throws an interesting cross-light upon his character. We think that Mr. Pickon is scarcely justified in wondering that Cavendish did not do more.

We are, in turn, surprised to find Bergman and Scheele spoken of as "two Swiss chemists of renown."

We learn that Lavoisier's refutation of the phlogiston hypothesis caused so much ill-will that he was burnt, in effigy, at Berlin. But his death, like Priestley's expatriation, was due to his having concerned himself with politics. The Republic certainly declared that she had "no need of savants," but, had Lavoisier been merely a *savant*, he might possibly have been overlooked by the leaders of faction.

It is something strange to find the atomic weight of platinum still given as higher than that of gold. In a table of the elements discovered this century, with the names of their discoverers, we have the names of workers observing and recognising bodies printed in italics, whilst "that of the observer" by whom the element was first isolated is printed in italicised capitals. In this manner, if we turn to thallium, we find "*Crookes*" merely given as recognising the existence of this metal, whilst to "*LAMY*" is awarded the honour of its first isolation.

All who desire a clear, readable, and, in the main, correct account of the rise and progress of chemical science, will find this book well suited to their purpose.

A Text-Book of Assaying: for the Use of Those Connected with Mines. By C. BERINGER, F.C.S., F.I.C., and J. J. BERINGER, F.C.S., F.I.C. London: C. Griffin and Co.

In the authors' preface we find reference to the definition of the term "assaying," as distinct from analysis. They do not agree with those authorities who restrict the term to dry processes for the determination of metals, nor with those who confine it to methods for the estimation of gold and silver. They consider that "the distinction between assayers and analysts will, in time, become difficult to detect." But why use two words for the same thing?

The work before us is, in fact, a general treatise on inorganic quantitative analysis, but with the addition of "dry," or "furnace," processes, which, save in the case of gold and silver, are not generally recognised.

As regards copper, the authors fully admit the unsatisfactory character of the Cornish assay, which, if we remember rightly, is totally proscribed in Chili. In many other instances, the authors admit the inaccuracy of the "dry" methods given.

We do not find any mention of the quantitative blow-pipe processes, which the authors may possibly have found unsatisfactory.

The rarer metals are not omitted, it being very justly remarked that their presence often modifies the behaviour of the common metals.

The separation and determination of the various metals associated with platinum are very briefly dealt with.

As an instance of the extraordinary comprehensiveness of the work, we may mention that there is a short notice of gas analysis, though with the reservation that it is not much used by assayers.

We find also a sketch of the sanitary examination of waters by the Nessler and the permanganate processes.

The instructions concerning "total solids" are drawn up with reference to mineral impurities, though we do not see any notice of the possible presence of phosphoric acid. We note the remark that "distilled water is only used by assayers in certain exceptional cases, so that by many it would be classed among the rarer oxides. Water of ordinary purity will do for most purposes, but the nature and quantity of the impurities must be known." We think this principle, which might be just as well extended to other reagents, is unsound and unsafe.

This work is an excellent manual, as far as the dry assays—where admissible—are concerned. As regards the other methods, the space at the disposal of the authors is, in many cases, insufficient.

Revised and Illustrated Catalogue of Apparatus for Technical Instruction. Part II., *Science and Technology*. Rigg's Technical Education Appliances, Limited, Bucklersbury.

This catalogue is exceedingly comprehensive, since it includes not merely apparatus required for instruction in the physical and natural sciences, but also lists of the works recommended by the Science and Art Department as text-books.

For the arrangement of the subjects the publishers, we presume, cannot be held responsible; otherwise we might venture to take exception to a classification which includes morphology under physiology, and confounds both with general biology. We find Dr. McAlister's work on the "Zoology of the Invertebrate Animals" (is there any zoology other than that of animals?) recommended under "Animal Physiology," whilst the same author's "Zoology of the Vertebrate Animals" comes in under "General Biology."

Morphology does not seem to be recognised by the Department as a "subject." Further, McAlpine's "Zoological Atlas" figures under Botany! Among the models (?) or diagrams for general biology we find No. 2214 "Butterflies of the silk-worm, male and female." This insect is generally considered, not as a butterfly, but as a moth!

That part of the catalogue which deals with chemistry and physics does not present any such sins against scientific method.

Energy and its Transformations: Mechanical Power, Heat, Light, Chemistry, Electricity, Magnetism. (L'Energie et ses Transformations: Mécanique, Chaleur, Lumière, Chimie, Électricité, Magnétisme). By R. COLSON, Captain of Engineers. Paris: Georges Carré.

This work reminds us of the "Correlation of the Physical Forces," by Sir W. R. Grove. The author, after explaining the primary conceptions of energy, work, and potential, considers the transformation of mechanical energy into heat, and the inverse process; the conversion of mechanical energy into light, with the reversal of this change. He shows that though chemical actions may be provoked by mechanical, thermic, or luminous energy, but without transformation of any of these energies into chemical energy—inversely, chemical energy may be transformed into thermic or luminous energy, but not directly into mechanical energy.

The third chapter is devoted to electricity, after which comes the question of the origin of energy. That this question is not solved, at least in its proper sense, is only what the reader must expect. The sun, we are of course told, maintains motion, activity, and life on the surface of the earth; but whence does it, in turn, derive its energy? Heat, light, chemism, electricity, and magnetism are next considered from the point of molecular mechanics.

In the concluding chapter we have reference to the

conservation of energy and the hypothesis of ether. But we scarcely see that the author has thrown any novel light on the arcana of the universe.

Chronic Bronchitis, and its Treatment: a Clinical Study.
By WILLIAM MURRELL, M.D., F.R.C.P. London:
H. K. Lewis.

THIS little work can be appreciated only by medical practitioners. We do not see that any point is raised upon which we are competent to form an opinion. Much of the treatment recommended turns on inhaling vapours; hence the author makes the practical suggestion that as "winter cough" is the commonest affection in the out-patients' department, a small room in every large hospital might be kept filled with the required vapour, so that a number of patients might be submitted to the treatment at once.

CORRESPONDENCE.

PENDULUM EXPERIMENTS AND GRAVITATION.

To the Editor of the Chemical News.

SIR,—I am obliged to Professor Boys for his criticism. This matter requires discussing, and by competent persons. He says it may interest me to know that the deviations are *many thousand times* as great as any that can be due to gravitation alone. Many thousand times as great would be ten thousand times at least, four or five thousand would be only several thousand. Let us see what this gives us:—We will take the ten-pound cylinder on the pendulum, and the five-pound cylinder fixed. The pendulum moves over an arc of seven thousandths of an inch; now, ten thousand times less than that will be seven ten-millionths of an inch! Can the Professor appreciate that length, or say that he knows that it is so? But we will not take many thousands, but only one thousand times, then the pendulum would pass over seven millionths of an inch; still many times less than can be appreciated.

Professor Boys suggests that the force of approach of bodies is complicated with magnetic force and electrification, besides these, with tilting and convection currents; these latter are effect and cause, and can affect only the Cavendish apparatus, the pendulum apparatus not at all.

The pendulum apparatus is made of brass and lead, which are not affected by magnetism. Why put that down as a source of complication?

As to electrification, it is well known that no piece of metal can be moved, but electricity will be induced if it cross the magnetic meridian at any angle; but the disturbance will be momentary at the beginning of the motion and at the end of it, but will cease instantly after the stoppage. The pendulum, of course, is liable to this; but then the motion is so small, never more than $\frac{1}{10}$ of an inch, and mostly $\frac{1}{20}$, and very slow, taking half a second, that the induction is so infinitesimal that it might be neglected, but it is not; the final measure is never taken till the pendulum is at rest. Thus, there is neither magnetic nor electric complications. The only force in action is the force which causes bodies to approach. With the Cavendish apparatus, electric induction is continual, for the beam is continually on the swing. But this is not the worst fault of that apparatus by a long way: the force of torsion cannot be weighed in the position in which it works, and to take it in any other position would give misleading results; besides, the torsion is not constant, the continued twisting and untwisting disturbs the molecular arrangement of the wire, and the variation of temperature alters the force of torsion; but

the worst fault is that one cannot get the real torsion to nearer than the one-hundredth of an inch. The beam has to be taken on the swing; for though one may have a graduated arc and a pointer passing over it, as I had, the central point of the swing cannot be ascertained to nearer than $\frac{1}{10}$ of an inch, under or over. All these defects make it an uncertain and unreliable apparatus; for these reasons I rejected it and devised the pendulum apparatus.—I am, &c.,

J. BAYNES THOMPSON.

DETECTING METALLIC SILVER IN THE PRESENCE OF LEAD.

To the Editor of the Chemical News.

SIR,—A far simpler and easier method of detecting silver in the presence of lead than that given by Mr. A. Johnstone, consists in adding to the nitric solution of the lead bead a few drops of a saturated solution of lead chloride, prepared by boiling a few grains of the salt with distilled water, allowing to cool, and decanting from the crystals. I called attention to this process and its use for quantitative purposes in the analysis of minium in your columns many years ago—so long that I have mislaid the reference.

The process consisted essentially in adding to a solution of pure nitrate of lead, of about the same gravity as the assay solution and containing lead chloride, a very dilute solution of nitrate of silver of known strength, until, on comparing the beakers on black cloth, the turbidity in the second beaker equalled that which had been produced by the lead chloride in the first.—I am, &c.,

THOS. P. BLUNT.

The Wyle Cop, Shrewsbury,
December 28, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 25, December 16, 1889.

The President announced that it is proposed to erect at the Conservatoire des Art et Metiers a statue in honour of Boussingault. M. Pasteur is President of the Committee.

The Colour and the Spectrum of Fluorine.—Henri Moissan.—If observed in a stratum of $\frac{1}{2}$ metre, fluorine possesses a distinct greenish yellow colour, fainter and more inclining to yellow than that of chlorine. If examined with the spectroscope in a stratum of 1 metre it does not present any absorption-bands. If a very small quantity of water is added to the fluorine in the tube, the water is decomposed, yielding hydrogen fluoride and ozone. The latter gas is produced in such a degree of concentration that the entire tube takes a deep indigo-blue colour. In a few minutes the ozone is destroyed and the blue colour is destroyed. The spectrum of fluorine, as obtained in a tube traversed by powerful sparks from a coil fitted with two condensers, comprises 13 rays in the red. With hydrogen fluoride we obtain several bands in the yellow and the violet, so indistinct and broad that their position could not be exactly determined.

Temperature of the Solidification of Arsenic Chloride and of Stannic Chloride, and their Power of Absorbing Chlorine at low Temperatures.—M. Besson.—Arsenic trichloride, if perfectly free from excess of chlorine, solidifies at -18° . If saturated with chlorine

at 0° it does not solidify above -30°. If saturated with chlorine at this temperature it congeals only at -60°. Stannic chloride freed from an excess of chlorine forms at -33° small white crystals. It absorbs large quantities of chlorine at low temperatures, whilst its solidifying-point rises.

Action of Ammonia on the Combinations of Mercury with the Chlorides.—Raoul Varet.—This paper does not admit of useful abstraction.

Adulteration of French Oil of Turpentine, and its Recognition.—A. Aignan.—The impurity added is resin oil, in the proportion of about 5 per cent. The fraud is detected by a determination of the rotatory power.

Synthesis of Dioxypiphenylamine and a Red-brown Colouring-matter.—M. Seyenitz.—The author obtains these results by heating resorcin in sealed tubes with 4 parts of ammoniacal calcium chloride.

Zeitschrift für Physikalische Chemie.
Vol. iii., Part 3.

The Transient Equilibrium of Atoms.—E. Pringsheim.—The endeavour to represent chemistry as the mechanics of atoms has caused it to be like physical mechanics divided into statics and dynamics. When Dalton put forward his atomic hypothesis, and when the chemical statics propounded by Berthollet thus became the doctrine of the equilibrium of atoms and molecules, the view was prevalent that atoms were in general at rest, and merely during the process of chemical transposition executed such movements as were necessary in order to pass from the position of rest, corresponding to the first chemical state, to that which they assume in the new body formed by the chemical transposition. Consequently, according to this view, the statics of atoms must be regarded as tantamount to the doctrine of ready-formed chemical compounds, whilst the dynamics of atoms represented the doctrine of compounds in course of formation or of chemical changes. But after the mechanical theory of heat had proved that the molecules are by no means at rest, but are constantly executing very violent movements, and after it was inferred with equal probability that the atoms also were in special motion within the molecule, chemists were obliged to develop new views as to the conditions of atomic movement in a state of chemical rest, and what changes of this movement correspond to a change in the constitution of the body in question. The simplest and formerly accepted theory is that the state of chemical rest is defined by the permanent continuance of each atom in its molecule, and that a chemical change occurs so soon as the individual atoms leave their molecules or several molecules combine to a single one. Another hypothesis regards chemical compounds as stable only when the mean condition of all molecules is alike, whilst the individual atoms travel constantly from one molecule to another. This theory, at which Williamson and Clausius arrived independently, proceeding from different points of view, is now shared by almost all thermochemists, at least in such a manner that they regard a great number of chemical states of rest as so-called conditions of movable equilibrium, in which simultaneously two (or more) chemical transpositions between the same elements are effected in such a manner that constantly so much of an existing chemical compound is decomposed to form another, as at the same time the second is decomposed for re-conversion into the first. If, therefore, we do not wish to come in collision with one of the best established physical disciplines, *i.e.*, the mechanical doctrine of heat and its consequence, the kinetic theory of gases we must no longer regard the state of chemical rest as a state of perfect atomic rest, but as a (in a wider sense) stationary movement of the atoms. Still it is possible to regard chemical rest as a state of equilibrium of the atoms (just as in mechanics we speak of a dynamic equilibrium), and consequently to retain the old conception

of chemical statics if we are able to indicate or even assume that these energies remain in equilibrium so long as the chemical compound remains unchanged, and that a disturbance of the equilibrium of these energies involves a chemical change. The only energies hitherto introduced into chemistry, those of affinity, by no means possess this property. If still the expressions "chemical statics and dynamics" and "equilibrium of atoms" are frequently used in their old significations, this persistence is harmless only if we remain conscious what meaning must be attributed to these terms according to the kinetic view. But although all chemists, generally speaking, are convinced of the special movement of molecules and atoms, this view is not yet sufficiently elaborated in detail, but with the old words old ideas have been retained. In most departments of chemistry a phenomenon is supposed to have been sufficiently explained by stating the arrangement of the atoms in a molecule, as though the atoms remained in unvarying positions. In many cases words and ideas are in use which cannot be readily accommodated to the new views, and even some which on these views are entirely unmeaning. As such, the author mentions the "transient equilibrium of atoms." He shows that those compounds which it was thought could be explained only by the assumption of a movable (*labile* as opposed to *stabile*) equilibrium of their atoms, do not differ qualitatively in the arrangement and the motion of their atoms from other chemical compounds which can be converted into other forms with liberation of energy.

Electro-chemical Thermo-dynamics.—Professor Willard Gibbs.—From the "Third Report of the British Association," p. 5.

On Aluminium Methyl.—Fr. Quincke.—The author's experiments, made by the process of gas-displacement, do not confirm the results of Louise and Roux; they testify decidedly against the existence of gas molecules of the form $Al_2(CH_3)_6$.

On the Magnitudes of the Affinities of Organic Acids and their Relation to their Composition and Constitution.—W. Ostwald.—This voluminous memoir, which is to be continued, does not admit of useful abridgment.

Relations between Osmotic Pressure, Depression of Freezing-point, and Electric Conductivity.—J. H. van't Hoff and L. Th. Reicher.—Between the two series of electric experiments there are only minimal differences which in the least favourable case (LiCl) do not reach 3 per cent. On the other hand, there exists between osmotic pressure and depression of the freezing-point an almost complete agreement, the greatest difference being only 4 per cent ($MgSO_4$). If the osmotic and electric numerical values are compared, an almost perfect agreement cannot be denied in the case of potassium and ammonium chlorides, calcium nitrate, and potassium ferrocyanide. It is somewhat different in magnesium sulphate and the remaining chlorides. The former shows, contrary to expectation, an unexpectedly small isotonic coefficient and a small depression of the freezing point; the latter, on the other hand, one unexpectedly great.

The Determination of the Latent Melting-heat by Depression of Freezing-point.—J. F. Eykman.—This paper consists chiefly of tables.

A Calculation of Atomic Refractions for Sodium Light.—Eugen Conrady.—This paper does not admit of useful abridgment.

The Molecular Volume of Sulphur.—H. Blitz.—A reply to Prof. Ramsay.

Journal für Praktische Chemie.
New Series, Vol. xl., 1889, Nos. 14 and 15.

Researches from the Laboratory of the University of Freiburg.—These consist of a paper by F. Kehrman

and O. Weichardt on some derivatives of nitronaphthalic acid, and a memoir by the former author on iodophenol-sulphonic acids and iodoquinones, with a preliminary notice of the second iodothymoquinone.

Reply to a Notice by A. Saytzeff.—K. Hazura.—A controversy of little scientific interest.

Moniteur Scientifique, Quesneville.
November, 1889.

New Application of Alkaline Sulphides in the Purification of Arsenious, Sulphuric, and Hydrochloric Acids.—Louis Ducher.—The author's process consists in the introduction of an alkaline or earthy-alkaline sulphide into the acid. The arsenic is precipitated by the nascent sulphuretted hydrogen produced. He prefers to use calcium or sodium sulphide, the former in the shape of vat-waste.

Nägeli's Amylodextrine and its Relation to Soluble Starch.—H. T. Brown and G. H. Morris.—From the *Journal of the Chemical Society*.

Behaviour of Phenolphthalein with Ammonia.—H. Long.—From the *CHEMICAL NEWS*.

The Formation of Incrustations in Marine Boilers.—V. Lewes.—From the *CHEMICAL NEWS*.

Examination of Feed-Water for Steam-Boilers.—Th. Bruce Warren.—From the *CHEMICAL NEWS*.

On the Compound $C_{21}Cl_{25}$.—E. Smith and H. Keller.—The authors, re-examining a portion of this supposed compound, found it fusible at 101° , and on analysis it yielded 2.2 per cent of hydrogen. They are still engaged with the investigation.

Estimation of Tannin in Tea.—J. Tsawoo White.—From the *CHEMICAL NEWS*.

Oxidation by Means of the Electric Current.—E. Smith.—From the *CHEMICAL NEWS*.

Application of the Same Method to the Separation of Mercury and Copper.—E. Smith and Lee Frankel.—From the *Journal of the Franklin Institute*.

On Chemical Affinity.—M. Pattison Muir.—From *Nature*.

Determination of the Molecular Weight of the Carbohydrates.—Horace T. Brown and G. Harris Morris.—From the *Journal of the Chemical Society*.

Report on a Research presented to the Academy of Medicine on the Physiological Action of Absinthe.—MM. Cadéac and Albin Meunier.—The conclusion which the authors draw from their careful experiments is that the genuine essence of absinthe is the most poisonous, and consequently the most dangerous, of all the substances sold under this name. It alone is capable of producing true epileptic attacks.

Dissociation of the Glycerides by Water under Pressure.—The author describes a thermodynamic apparatus invented by M. Hughes, and now in action at the Stearine Works de l'Etoile. It consists of an upright autoclave of copper, in which 1000 kilos. of a mixture of tallow and palm oil is treated at once. Steam at a pressure of 14 to 15 atmospheres is carried to the bottom of the autoclave by a plunging tube. After six to seven hours of treatment there remains only about 5 per cent of neutral matter, the dissociation of which is completed by means of sulphuric acid. The watery glycerin, at 3° Baumé, is concentrated by means of the waste steam up to the standard of 28° B.

The Life-Work of a Chemist (M. Pasteur).—A discourse delivered by Sir H. E. Roscoe at the Birmingham and Midland Institute.

Recent Improvements in the Manufacture of Chloroform.—S. P. Sadler.—From the *Pharmaceutical Journal*.

Influence of Temperature on the Specific Rotation of Cane-Sugar.—Clement W. Andrews.—From the *Technological Quarterly*.

Industrial Review of Various Patents.—Abstracts of the specifications of a number of German patents.

MISCELLANEOUS.

An Appeal.—Mr. A. McDonald Graham died about two years ago, after a long illness, leaving a widow and several children quite without means of support. Mrs. Graham has had an operation, which restored somewhat her failing eyesight, but since the operation she has suffered from erysipelas, and is completely prostrated and in actual want. Donations may be made to Messrs. MAY AND BAKER, Garden Wharf, Battersea, London.

Donations received:—

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University College, Liverpool.—The Sheridan Muspratt Chemical Scholarship, of the value of £50 for two years, has been awarded to Mr. J. T. Conroy, who has been a student in the chemical laboratories during the past two years. Mr. Conroy has recently taken the degree of B.Sc., with Honours in Chemistry, at the University of London. The Scholarship, which is the gift of Mrs. Sheridan Muspratt, is intended to enable the holder to continue work in the higher branches of chemistry. The Sheridan Muspratt Exhibition of £25 has been awarded to Mr. A. Carey, of Widnes, who has been a student of the College during the last two and a half years, and is now in the final stage of preparation in the Honours School of Chemistry of Victoria University.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Medical, 8.30.
Society of Chemical Industry, 8. "Peroxide of Hydrogen; its Preservation and Commercial Uses," by C. T. Kingzett, F.C.S. "An Analytical Tintometer," by Mr. Lovibond.
TUESDAY, 7th.—Royal Institution, 3. "Electricity," by Prof. A. W. Rücker, F.R.S.
WEDNESDAY, 8th.—Geological, 8.
Microscopical, 8.
THURSDAY, 9th.—Royal, 4.30.
Royal Society Club, 6.30.
Royal Institution, 3. "Electricity," by Prof. A. W. Rücker, F.R.S.
Mathematical, 8.
Institute of Electrical Engineers, 8.
FRIDAY, 10th.—Quekett Club, 8.
Astronomical, 8.

ENTRIES CLOSE WEDNESDAY, 15TH INST.

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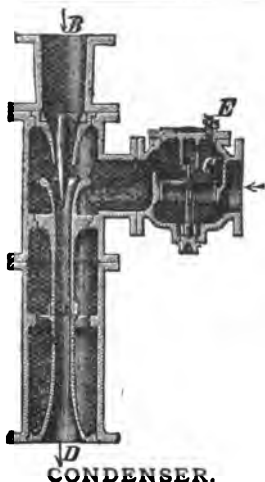
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London: Printed and Published for the Proprietor by EDWIN JOHN DAVY, at the Office, Boy Court, Ludgate Hill, E.C.
January 3, 1890.

THE CHEMICAL NEWS.

VOL. LXI. No. 1572.

NOTE ON THE COLORIMETRIC METHODS FOR THE DETERMINATION OF NITRATES IN POTABLE WATERS.

By A. E. JOHNSON, F.I.C., F.C.S.
Associate of the Royal College of Science.

UNDER the above heading Dr. S. Rideal gives, in the *CHEMICAL NEWS*, vol. lx., p. 261, an account of the "phenol sulphuric acid" method for determining nitrogen as nitrates in water—a method originally introduced, I believe, by Dr. Sprengel. This extremely useful and accurate method I have had in constant use in the laboratory for the past seven years. I have proved that the results obtained by its means agree exactly with those obtained by Crum's well-known method. The solutions I use, however, are somewhat different from those described by Dr. Rideal.

In the first place I make my standard solution of potassic nitrate as follows. 0.7215 grm. KNO_3 crystals is dissolved in a litre of distilled water. 100 c.c. of this solution is then diluted to a litre with distilled water, and this diluted solution is always used as the standard of comparison, 10 c.c. being most frequently measured out. 10 c.c. of this solution contain N equivalent to 1 part of N as nitrates in 100,000. This will, I think, be generally admitted to be a better solution than Dr. Rideal's, of just ten times the strength, as the errors of measuring so small a quantity as 1 c.c. are avoided.

Secondly, as to the phenol sulphuric acid solution. Dr. Rideal's solution differs from mine both in the relative proportions of phenol and sulphuric acid used, and also in no HCl being used by Dr. Rideal, whilst this is an important factor in giving delicacy of action to my solution. On this point I may quote Mr. D. Lindo as epitomised in the *J. Chem. Soc.* for 1888, p. 1338, the original papers having appeared in the *CHEMICAL NEWS*. The abstractor says "Phenol alone appears to be but a poor test for nitrates, but in the presence of hydrochloric acid it becomes very delicate." Dr. Rideal, moreover, simply mixes his phenol and sulphuric acid, whereas I have found it absolutely essential to digest the mixture for several hours, otherwise the finished solution gives a green instead of a yellow liquid with nitrates. My solution is made as follows:—Two parts by measure of pure crystallised phenol—liquefied by heat—are poured into five parts by measure of pure concentrated H_2SO_4 and the whole digested in a water-bath kept boiling for eight hours. Allow to cool and add $1\frac{1}{2}$ volumes of distilled water and $\frac{1}{2}$ vol. strong HCl to each volume of the above mixture. Convenient quantities are 80 c.c. phenol, 200 c.c. H_2SO_4 , 420 c.c. OH_2 , and 140 c.c. HCl, producing 840 c.c. of a light brown solution, which is ready for immediate use. The water residue does not require treating with water and sulphuric acid separately, but with this solution only.

My method of procedure, which is very simple, is as follows:—10 c.c. of the water under examination and 10 c.c. of the standard potassic nitrate are pipetted into two small beakers and placed near the edge of a hot plate. When nearly evaporated they are removed to the top of the water-oven and left there till they are evaporated to complete dryness. As this operation usually takes about an hour and a half, it is better when time is an object, to evaporate to dryness in a platinum dish over steam. The residue in each case is then treated with 1 c.c. of the phenol-sulphuric acid, and the beakers are placed on the top of the water-oven. If the water under examination

contain a large quantity of nitrates the liquid speedily assumes a red colour, which, in a good water, will not appear for about ten minutes. After standing for fifteen minutes the beakers are removed, the contents of each washed out successively into a 100 c.c. measuring glass, a slight excess (about 20 c.c. of 0.96) of ammonia added, the 100 c.c. made up by the addition of water, and the yellow liquid transferred to a Nessler glass (6 in. $\times$ 1 $\frac{1}{2}$ in.). The more strongly coloured liquid is then partly transferred to the measuring-glass again and the tints compared a second time. In this way the tints are adjusted, and when, as far as possible, matched, the liquid that has been partially removed is made up to the 100 c.c. mark with water, and, after well mixing, finally compared. If not exactly the same, a new liquid can at once be made up, probably of exactly the same tint, as the first experiment gives very nearly the number of c.c. of the one equivalent to the 100 c.c. of the other. In my "Analyst's Laboratory Companion," p. 50, I have given a very useful table for obtaining it in parts per 100,000, and also in grains per gallon, by this method.

In the case of very good waters, 20, 50, or more c.c. should be evaporated to a small bulk, rinsed into a small beaker, and evaporated to dryness and treated as above—only 5 c.c. of the standard potassic nitrate (= 0.5 N in 100,000) being taken. In the case of very bad waters, 10 c.c. should be pipetted into a 100 c.c. measuring flask and made up to the mark with distilled water; then 10 c.c. of the well mixed liquid (= 1 c.c. original water) withdrawn and treated as above.

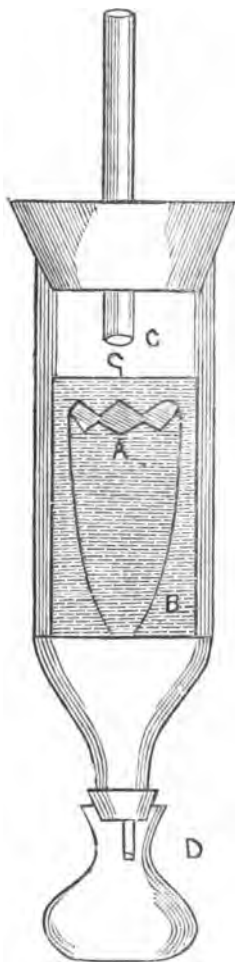
AN ACCURATE AND SPEEDY METHOD OF EXAMINING MEAT EXTRACTS AND OTHER SUBSTANCES OF AN ALLIED NATURE BY MEANS OF THE NEW PLATINUM EXTRACTION APPARATUS

By H. N. WARREN, Research Analyst.

THE various meat extracts of commerce all depend more or less, as far as their dietetic value is concerned, on what is known as the percentage of soluble extract; or, in more technical terms, the relative amount of extract soluble in alcohol of 80 per cent. In order to accomplish this it is requisite to dry the sample until constant, either by the aid of a water-bath or hot air steriliser maintained at the desired temperature. To now extract the dried residue by means of alcohol, and thus obtain a general estimate of its solubility, is void of any difficulty; but to arrive at a true percentage presents an entirely new feature, inasmuch that so obstinate are the gumming or solidifying properties of the remaining portion that any ordinary process, such, for instance, as the employment of a Soxhlet's tube or any form of apparatus where a limited supply of alcohol only is attainable, remains perfectly inadequate.

The following form of apparatus, which is illustrated by the accompanying diagram, and which I am about to briefly describe, invariably results in the formation of a larger percentage of soluble extract than the various other extractors with which I have compared it, both an account of the large bulk of alcohol that is continuously brought to play upon the enclosed residue, and at the same time retaining a much higher temperature, and, by so doing, performing the operation in less than half the usual time. A brief summary will suffice to explain the construction of the same:—A is a tared paper which has been previously treated with alcohol. Into this is placed the dried extract, to which has been added a small quantity of carefully prepared and weighed sand, and the whole introduced into the platinum cage, B, which is readily contrived by coiling in a spiral manner a piece of platinum gauze, turning inwards the lower ex-

teremities in order to form a bottom, and furnishing the same with a cap surmounted by a small hook, while the whole is maintained in position by surrounding the same by means of the glass tube, c, and in direct connection with the flask, d, and containing the requisite amount of alcohol, the entire apparatus being connected by the usual method to a Liebig's condenser, whence a rapid and effectual distillation is readily accomplished. The platinum cage thus acting twofold, both by retaining any paper that may become mechanically detached by means of the alcohol, and at the same time preventing the paper from becoming attached to the sides of the outer or retaining tube, and, by so doing, retarding the influx of alcohol. In cases where the weight of residue is required it forms a



most effective and simple arrangement, being readily detached from the glass tube when required, and admitting of being readily weighed by suspending it from the beam of a balance by means of the small hook provided at the summit. In certain instances where the inorganic portion is required it may be readily ignited without detaching the residue and the amount estimated.

In the performance of milk analysis a rapid and accurate determination may be made as follows, a sufficiency of the sample having been evaporated in a platinum dish to a convenient bulk. A known quantity of sand which has been thoroughly purified and tared is placed in a paper or fine linen filter and the milk poured into the same, the sand at once retaining without risk of loss the whole of the evaporated sample, which, after drying until

constant, and deducting superfluous substances, gives the total percentage of solids: or it may be divided into two portions, using the residue for extraction of fat only, relying upon a second portion for estimation of solids.

With reference to sand I may also state that I have frequently used with success prepared sponge as an absorbing agent.

The following figures have been actual results obtained when in comparison with other methods, using, in each instance, the same amount of alcohol and an equal duration of time, those marked A, B, C, being results obtained by the platinum apparatus, while those marked D, E, F are results obtained by the usual extractors.

A.	
Extract soluble in alcohol at 80	
per cent	54'36
Insoluble	26'18
B.	
Soluble extract	59'98
Insoluble	20'20
C.	
Soluble extract	41'63
Insoluble	19'15
D.	
Extract soluble in alcohol ..	54'01
Insoluble	26'53
E.	
Soluble	59'56
Insoluble	20'62
F.	
Soluble	41'11
Insoluble	19'67

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THE APPLICATION OF DOUBLE PYROPHOSPHATES FOR THE ELECTROLYTIC SEPARATION AND DETERMINATION OF METALS.

By Dr. ALBANO BRAND.

(Continued from p. 4).

In acid solutions only the double manganic pyrophosphate is formed without undergoing a decomposition; whilst in a sulphuric solution it remains permanent during the entire duration of the electrolysis; in a strongly nitric solution the reductive action soon preponderates, for the liquid after a time becomes again colourless.

In the electrolysis of the double manganese-ammonium salt in an excess of the precipitant there is formed, with currents of all strengths, merely the double manganic salt, without undergoing a decomposition, and the solution, according to the proportion of manganese, takes a colour ranging from a pale rose to a deep claret.

From these solutions the manganese cannot be separated quantitatively, but its determination succeeds very well if ammonia is added.

From the strongly ammoniacal solution of the double manganese sodium salt, in case of weak currents the manganese separates as peroxide, adhering firmly to the anode; the liquid no longer turns brown, but the formation of the red manganese salt does not entirely cease until about 15 per cent of strong ammonia is added to the solution.

In the preparation of the electrolyte only so much sodium pyrophosphate is used as is fully sufficient for the formation of the double salt, and the precipitate is redissolved in ammonia. The platinum capsule is conveniently used as positive electrode, and if but little man-

ganese is present (0.02 grm. Mn in 100 c.c.), a current is used of 0.1 c.c. detonating gas per minute; if more manganese is present the strength of the current is reduced at the beginning (0.01 c.c. if 0.1 grm. Mn in 100 c.c.). From a solution of 200 c.c. 0.2 grm. manganese can be conveniently deposited as peroxide upon a platinum capsule of 150 c.c. surface. The strength of the current towards the end must not be increased above 0.4 c.c., since with stronger currents gas is liberated and separates the deposit from the capsule.

As the precipitate must be well washed, in order to remove all non-volatile salts, it is well not to try to keep all the deposit adhering to the capsule. All the flakes which become detached are collected upon a small filter free from ash, which is then burnt in the capsule. Only distilled water must be used in washing, since the use of alcohol causes the entire precipitate to become detached.

The conversion of the hydrated manganese peroxide into manganic oxide is effected more rapidly over the blast than over a Bunsen. An oxidising flame gives good results.

5. *Zinc*.—The white gelatinous precipitate of the zinc salts dissolves readily in an excess of the precipitant and behaves normally. In these solutions soda-lye produces a precipitate insoluble in excess.

For the determination of zinc, a solution of the double salt mixed with ammonia (or, better, with ammonium carbonate) is suitable, and the metal is deposited in an adhesive condition and of a zinc-grey colour. If much zinc is present (0.2 grm. or upwards) the bulk is thrown down with a current of 5—10 c.c. detonating gas per minute, but for the completion of the reduction a current of 15—20 c.c. is needed. An anode of wire yields a more uniform deposit than one of sheet metal. As in the case of iron, the deposit must be washed without interrupting the current.

The author has several times—though not invariably—succeeded in dissolving off the deposit of zinc from a platinum capsule (not, of course, from silver or tin) in cold strong aqua regia, so as to leave no residue; the capsule is not attacked.

If the electrolyte contains both zinc and iron, the zinc, as in the case of the double oxalates, is completely deposited only if the iron is in large excess.

6. *Cadmium*.—The white cadmium salt deposited on the addition of sodium pyrophosphate is soluble in a large excess of the precipitant. It is easily dissolved in ammonia, but on the addition of ammonium carbonate there appears a precipitate. The double ammonium salt is more soluble, but is subsequently re-deposited; with ammonia and ammonium carbonate it behaves like the sodium salt.

The sparing solubility of the double sodium salt was an inducement to effect solution by the addition of acids.

From a solution in vitreous phosphoric acid, or sulphuric acid (less than 1 vol. per cent), the metal is deposited by a current of 0.2—0.5 c.c. detonating gas per minute, of a bluish white colour, but it has some tendency to become spongy. The phosphate, dissolved in vitreous phosphoric acid, gives better deposits.

After the addition of a little nitric acid, the metal requires for reduction the current of two to three Bunsen elements.

If the solution contains from 1 to 2 per cent (by volume) of strong sulphuric acid, the metal is deposited by a current of 0.2—1.0 c.c. in a white adhesive and distinctly crystalline condition. If the current, towards the end of the process is increased to 5—10 c.c., the reduction is quantitative. In presence of more than 1 per cent of sulphuric acid, only the sulphate, but not the pyrophosphate, is electrolysed.

The ammoniacal solution of the cadmium pyrophosphate is especially adapted for the quantitative separation of cadmium.

An abundant addition of ammonia is required, otherwise the salt is again separated out on electrolysis. In

order to overcome the strong polarisation, the decomposition is initiated by a current of 2—3 c.c. acting for a few seconds. Then a current of 0.3 to 1 c.c. is allowed to act until the bulk of the metal is deposited, and at the end the decomposition is accelerated by raising the current to about 5 c.c. The metal deposited is dense and of a silvery white colour, and perfectly smooth to the touch. If the initial current is stronger, tufted crystals are readily formed.

Cadmium is precipitated from its double pyrophosphates by sulphuretted hydrogen, but as this reaction is not sufficiently delicate for traces, the end of the reaction is best ascertained by the absence of deposition on fresh parts of the platinum capsule.

7. *Copper*.—The whitish blue precipitate appearing in solutions of copper salts is quite normal in its behaviour. It dissolves readily in an excess of the precipitant. On the addition of ammonia or ammonium carbonate the light blue solution becomes a dark blue.

The solutions of the double pyrophosphate are little suited for the determination of copper. From a solution mixed with ammonia, and still more with ammonium carbonate, the copper is separated out in a dense state only with very feeble currents; with stronger currents it is apt to become pulverulent. The solution of the copper salt in an excess of the precipitant, and without any further addition, is most suitable. A current of 0.1 c.c. detonating gas per minute, increased at the end to 1 c.c., throws down the copper in an adhesive metallic state, though of a dirty red colour.

If the solution of the double salt is mixed with sulphuric or nitric acid, the presence of the pyrophosphoric acid does not disturb the process, and the copper is deposited with its usual metallic properties.

8. *Silver*.—The white silver pyrophosphate is almost insoluble in an excess of sodium pyrophosphate, but readily soluble in ammonia and ammonium carbonate. The silver salt precipitated by ammonium pyrophosphate is soluble in an excess of the precipitant and in ammonium carbonate, but is re-precipitated by ammonia.

From a solution of the silver-sodium pyrophosphate in ammonia, or in ammonium carbonate, the silver is readily separated by a current of 0.01 c.c., but has a disposition to become spongy.

For a quantitative determination, we may use the electrolysis of a solution of the sodium double salt, faintly acidulated with nitric acid, by a current of 0.1 c.c. detonating gas per minute, increasing towards the end to 0.2 c.c.; but this solution offers no advantages as compared with a potassium cyanide solution.

9. *Mercury*.—Mercurous salts yield, with the sodium and ammonium pyrophosphates, a white precipitate readily soluble in an excess of the precipitant. In this solution ammonia, ammonium carbonate, and many other salts produce a black-grey precipitate; a similar decomposition is also produced by boiling or by electrolysis.

Mercuric salts give with sodium pyrophosphate a precipitate insoluble in an excess of the precipitant, but readily soluble in ammonia or ammonium carbonate. The mercuric nitrate, of which H. Rose and A. Schwarzenberg stated that the white precipitate first formed is turned reddish yellow or yellowish red by an excess of sodium pyrophosphate, behaves in a similar manner if the saline solution contains so much nitric acid that it has still an acid reaction after the addition of the sodium pyrophosphate necessary for the formation of the double salt. The salt precipitated by ammonium pyrophosphate is soluble in a large excess of the precipitant, but behaves otherwise like the sodium salt.

For quantitative determinations the most suitable are the solutions of the double mercuric salt in ammonia or ammonium carbonate; mercurous salts must previously be converted into the mercuric state.

The reduction of the double mercuric salt is effected by currents of all strengths. With a current giving 2 c.c. detonating gas per minute, 1 grm. of the metal can be

quantitatively deposited in five to six hours. The reduction is complete when a few c.c. of the electrolyte no longer give a precipitate with ammonia.

After pouring off the liquid the metal is washed with distilled water, alcohol, and ether, and dried for a short time over sulphuric acid in the exsiccator.

(To be continued.)

A DESCRIPTION OF SEVERAL YTTRIA AND THORIA MINERALS FROM LLANO COUNTY, TEXAS.*

By W. E. HIDDEN and J. B. MAXINTOSH.

(Concluded from p. 9).

THORO-GUMMITE, a Hydrated Uranium Thoro-Silicate.

THIS mineral, of which we have been able to gather about one kilo., occurs intimately associated with fergusonite and cyrtolite, and masses up to three ounces have been found, though for the most part it is in very small pieces. It is of a dull yellowish brown colour, has hardness above that of gummite, or 4-4.5, and occurs commonly massive, though several well-defined groups of zircon-shaped crystals have been discovered with angles near to those of zircon. It has a characteristic colour, after ignition, becoming of a dull greenish hue, thus it is distinguished from freyalite, eucrasite, and thorite, which species it otherwise resembles in some respects. Its specific gravity varies from 4.43 to 4.54. It is easily soluble in nitric acid. The analytical results are:—(See Table I.)

Regarding phosphorus as non-essential and as combined with the slight excess of uranium, above that which is required by the formula which we derive, and with the undetermined and lost constituents, we get the oxygen ratio of $\text{UO}_3 : \text{SiO}_2 : \text{ThO}_2 : \text{H}_2\text{O} = 1 : 2 : 2 : 2$. The last three terms are in the proportion required by thorite, and we see that the molecule of the mineral may be regarded as made up of three molecules of thorite linked together by one of uranic oxide, forming a compound molecule, which at first sight seemingly complex, is really of great simplicity.

Using graphic notation, the formula of the mineral is $\text{UO}_6(\text{ThOSi})_3(\text{OH})_{12}$, or when written in the usual manner $\text{UO}_{3.3}\text{ThO}_{2.3}\text{SiO}_{2.6}\text{H}_2\text{O}$. The thorium and silica bear the same relation to the uranium, and it seems better to regard the mineral as a hydrated thoro-silicate of uranium, rather than as a urano-silicate of thorium, or as a double silicate of uranium and thorium, if, indeed, we might not go further and consider the whole as a duodeci-atomic molecule of a complex inorganic acid. We name this mineral *thoro-gummite*, because it is a gummite in which the water has been replaced by the thorite molecule.

NIVENITE, a Hydrated Thorium-Yttrium-Lead Uranate.

THIS mineral we found intimately associated with fergusonite and thoro-gummite. It is as yet a rare mineral at the locality. Its specific gravity is 8.01. $H = 5.5$. It is velvet-black in colour, and when powdered becomes brown black. After ignition it turns blue-black. As yet only massive pieces have been found, but some of these suggest that the species may be isometric in crystallisation. It is easily soluble in nitric and sulphuric acids, and some slight effervescence† was noticed upon dissolving the mineral. The analysis gave the following results:—(See Table II.)

The ratios found lead to the general formula—



in which, RO may be replaced by its equivalent in R_2O_3

and RO_2 . If the iron be calculated as protoxide, and a corresponding increase be made in the amount of uranic oxide, the ratio for $\text{UO}_3 : \text{RO} : \text{H}_2\text{O}$ becomes 12 : 8.74 : 3.40. As it was not possible to determine the state of oxidation of the iron in presence of the two oxides of uranium by any process known to us, we cannot give the exact ratio, as it exists, but would point out that if only 0.33 per cent of ferric oxide is present and the rest of the iron is present as protoxide, then the ratio of UO_3 to bases will be exactly that which is required by the formula.

This mineral is allied to the rare species cleveite* and bröggerite,† and we give below the analysis with the formulæ which we have calculated from them, so that the points of distinction may be made evident. (See Table III.)

In the bröggerite analysis a small amount of silica occurs, which if supposed to exist as admixed silicate will reduce the excess of basic oxygen. Neglecting the water in bröggerite the oxygen ratio for these minerals will be therefore:—

	Bases. $\text{RO}_2(\text{R}_2\text{O}_3\text{RO})$	UO_3	H_2O
Cleveite	1	2	1
Bröggerite	1	1	

The comparison of the three formulæ shows the relationship clearly (RO including RO_2 and R_2O_3), as follows:—

Bröggerite	3RO, UO_3 .
Cleveite	6RO, 2UO_3 , $3\text{H}_2\text{O}$.
Nivenite	9RO, 4UO_3 , $3\text{H}_2\text{O}$.

We have named this mineral *nivenite*, in recognition of the energy which Mr. Niven has displayed at this locality, and the assistance which he rendered us in obtaining the mineral for investigation.

FERGUSONITE.

THIS heretofore rare mineral occurs in large quantity at this new locality. Up to this date we have received over seventy kilos., some masses of which weighed over a pound. Broken prisms, rough in form, rarely showing terminal planes, and masses of crystals interlacing each other in the manner of occurrence. The immediately associated minerals are cyrtolite and thoro-gummite and also magnetite. The gadolinite also sometimes encloses it. It also occurs alone in a matrix of orthoclase or of quartz. One large mass of this kind of gangue, upon being broken up, yielded over thirty kilos. of pure mineral in the form of fragments, most of which were basal sections of crystals which had been originally four to eight inches long and about $1\frac{1}{2}$ c.m. thick.

We have found two distinct varieties, of which we here append analyses and description.

Fergusonite, Mono-Hydrated.—Specific gravity = 5.67; hardness 6-6.5; forms tetragonal, with acute octahedral terminations, a zirconoid plane hemihedrally developed, and, rarely, the basal pinacoid. The crystals are rough and dull grey exteriorly, but with a bronzy sub-metallic appearance on the surface of fracture, which is small, conchoidal, and brilliant. Thin splinters show a yellowish brown translucence; colour bronzy hair-brown; streak and powder dull brown. It is infusible, but on ignition the powdered mineral changes to a pale olive-green colour, and a momentary glow creeps over the mass at the point of redness. Fragments decrepitate violently when heated. With a microscope a peculiar light brown muddiness is noticed, and the mineral is filled with minute streaks and spots of a darker shade, all of which may indicate incipient alteration.

Crystals often have a thin coating of, or are otherwise partly altered to, the tri-hydrated variety, next described. It is decomposed when in fine powder by hydrochloric

* From the *American Journal of Science*, Third Series, vol. xxxviii., No. 228, December, 1889.

† Cf. Hillebrand, who has identified nitrogen in uranite, *American Journal of Science*, Oct. 1889, p. 329.

* Dana's Appendix, III., p. 28.

† *American Journal of Science*, June, 1884, p. 493.

TABLE I.

			Oxygen ratio.
SiO ₂	13.085		43.62 = 2.000
UO ₃	22.43		23.37 = 1.071
ThO ₂	41.44		
Al ₂ O ₃	0.965	31.22	} 43.64 = 2.001
Fe ₂ O ₃	0.845	2.83	
(CeY) ₂ O ₃ , &c.	6.69	1.59	
PbO	2.16	6.30	
CaO	0.41	0.97	} 43.78 = 2.008
H ₂ O	7.88	0.73	
P ₂ O ₅	1.19		
Moisture	1.23		
	98.325		

Atomic weight = 135

TABLE II.

			Oxygen ratio.
UO ₃	46.75		48.69 = 12.
UO ₂	19.89	14.62	} 37.33 = 9.20
ThO ₂	7.57	5.74	
Y ₂ O ₃ , &c.	11.22	11.34	
Fe ₂ O ₃	0.58	1.08	
PbO	10.16	4.55	} 14.11 = 3.48
(Ignition) loss H ₂ O	2.54		
Insoluble	1.22		
	99.93		

Atomic weight 124.2

TABLE III.

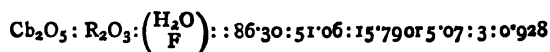
Cleveite.				Bröggerite.			
Specific gravity = 7.49.				Specific gravity = 8.73.			
	Per cent.	Oxygen ratio.		Per cent.	Oxygen ratio.		
UO ₃	42.04	43.79		38.82			
UO ₂	23.89	17.56	} 42.16	41.25	30.33	} 34.61	} 44.18
ThO ₂	4.76	3.61		5.04	4.28		
Y ₂ O ₃	6.87	9.03		2.42	3.18		
Er ₂ O ₃	3.47	2.73		—	—		
Ce ₂ O ₃	2.33	2.16	} 20.99	0.35	0.33	} 9.57	
Fe ₂ O ₃	1.05	2.00		—	—		
FeO	—	—		1.26	1.75	} 3.77	
CaO	—	—		0.30	0.54		
PbO	11.31	5.07		8.41	3.77		
SiO ₂	—	—		0.81	2.70	} 4.61 (negled)	
H ₂ O	4.28	23.78		0.83	4.61 (negled)		
	100.00			100.09			

acid, with separation of columbic acid. The analytical results are as follows:—

		Oxygen ratio.	
Cb ₂ O ₅	46.27	86.30	
UO ₃	1.54	1.59	
ThO ₂	3.38	2.56	
Al ₂ O ₃	0.09	0.27	
Fe ₂ O ₃	0.98	1.83	
(A) Y ₂ O ₃	23.95	26.70	} 52.65
(B) Y ₂ O ₃	18.38	20.07	
PtO	1.43	0.64	
ZnO	0.24	0.30	
CaO	0.10	0.18	
MgO	0.04	0.10	
Ignition H ₂ O	1.98	11.00	} 15.79
110° C. H ₂ O	0.04	—	
F	0.91	4.79	
	99.33		
Less O = F	0.38		
	98.95		

Atomic weights, 110.55
Atomic ratio

Counting UO₃ as combined with a portion of the bases in the proportion R₂O₃—UO₃, we have for the oxygen ratio of the other constituents, counting fluorine as replacing hydroxyl,—



This leads to the formula Cb₂O₅.R₂O₃.H₂O; or if bases are counted as RO then R₃Cb₂O₇(OH,F)₂.

We tested the columbic acid for titanate acid and tin, but, although we obtained small quantities of precipitates, they proved to be largely, if not altogether, columbic acid, and we did not detect the presence of any other substance. Tantalate acid was not looked for.

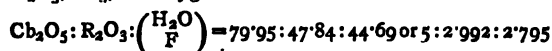
Fergusonite, Tri-Hydrated.—Specific gravity = 4.36—4.48; hardness about 5; colour deep brown, almost black, thin edges show a yellowish brown translucence; form and exterior appearance same as the species previously described; streak and powder pale greenish grey; on ignition turns light brown, but does not glow or decrepitate like fergusonite; is decomposed by hydrochloric acid, with separation of columbic acid.

* Total Y₂O₃, &c., and Ce carths = 42.33

Analysis.

		Oxygen ratio.
Cb ₂ O ₅	42.79	79.95
UO ₃	3.12	3.24
UO ₂	3.93	2.90
ThO ₂	0.83	0.62
Al ₂ O ₃	0.85	2.49
Fe ₂ O ₃	3.75	7.03
Y ₂ O ₃ , &c. ..	31.36	32.28
PbO	1.94	0.87
CaO	2.74	4.89
Ignition H ₂ O ..	7.57	42.05
110° C. H ₂ O ..	0.62	—
F	0.502	2.64
		44.69
	Atomic weight, = 121.77	
	Atomic ratio	
100.002		
Less O = F ..	0.206	
	99.796	

Combining UO₃, as before, with bases to form R₂O₃, UO₃, the oxygen ratio of the remainder will be—



This gives the formula Cb₂O₅.R₂O₃.3H₂O, or counting bases as RO, then R₃Cb₂O₅(OH.F)₆. On comparing the properties of the two minerals here described with typical fergusonite we notice a graduation from the one extreme to the other.

		Specific gravity.	Hardness.	When heated.
Fergusonite.	R ₃ Cb ₂ O ₈	5.838 (?)		
Mono-hydro-fergusonite	R ₃ Cb ₂ O ₇ (OH) ₂	5.67	6.5	Pale olive-green decrepitate.
Tri-hydro-fergusonite	R ₃ Cb ₂ O ₅ (OH) ₆	4.36-4.48	5.	Light brown, does not decrepitate.

Of other published analyses of fergusonite, that of the Ytterby variety, by Nordenskiöld ("Dana's System Min.," p. 523), corresponds to the di-hydrated mineral. Since we find fluorine in the specimens we have analysed from Texas, we are led to conclude that the water is not present as water of crystallisation, but as hydroxyl which is partially replaced by the fluorine, and this being so, we consider that the name fergusonite should be reserved for the anhydrous mineral, and that the various definite alteration products, with two, four, six, and perhaps more hydroxyls, should be distinguished in some manner, either by prefixing mono-hydro, di-hydro, &c., or by special names. It seems better that the first method of distinguishing them should be followed. We believe that we have observed a still higher alteration product in traces on some of the specimens we have obtained from Texas.

Allanite has not as yet been found very abundantly at this locality, and all of the ten kilos. obtained was massive-nodular in form. Its surface alteration is very slight compared with that of the other allied minerals. Its colour is shining pitchy black. Powder and streak dull greenish brown. Upon ignition it first turns red-brown and then becomes coal-black. It is opaque, except in the very thinnest splinters, when a greenish brown translucence is evident. Specific gravity = 3.488. We have made no complete analysis as yet, but the specimen tested showed the presence of considerable quantities of the cerium-yttrium earths and of thoria, and we learned that it was completely soluble in acids, with separation of gelatinous silica, either before or after igniting the mineral (like the associated gadolinite). The better masses have been found quite isolated from the other occurring minerals.

Molybdenite occurs sparingly in quite large folia, and

in hexagonal tables, with the cyrtolite and fergusonite. Only a few ounces have been collected.

Molybdenite was noticed in the cavities once occupied by molybdenite, and it often yet retained the plate-like form of the mineral from which it was derived by alteration. Its colour was white to greenish white. Specific gravity = 4.004. On two specimens indistinct crystals have been found, having a light apple-green colour and almost perfect transparency. Qualitative tests have shown the absence of any large amounts of anything but molybdenic acid.

Cyrtolite has been found abundantly in both massive form and in good crystallisations. One hundred kilos. have thus far been collected while mining the yttria minerals already herein described. This mineral here occurs in thick plates attached to the biotite and also constituting veins in the coarse pegmatite. It is often the matrix of the thoro-gummite and fergusonite. Specific gravity = 3.652. It occurs in tetragonal forms, with all the planes rounded, and polysynthetic groupings of crystals are very common. Its colour ranges from dull grey, through various shades of brown to deep brown and almost black. Hardness about 5. We shall defer further mention of this mineral until we have examined it more thoroughly.

Fluorite occurs in some abundance. Masses of a pale greenish kind were found, weighing fifty pounds, tightly embedded in the pegmatite. Purple and white shades have also been found. A very opaque dark purple kind has been found in small masses. Its property of phosphorescing (green) when gently heated has given rise to a great local interest in this particular mineral.

Gummite occurs sparingly, but we have not as yet been able to find it in a sufficiently pure condition for examination. Several varieties have been seen, and "yttrium-gummite" is very probably one of them.

Tengerite (?)—In the cracks and fissures of the gadolinite and yttrialite a white mineral, rich in CO₂, is often noticed. We have seen it in globular radiated incrustations and in one instance in distinct transparent isolated crystals. Dr. Gentz has already noted its occurrence, and, as he observes, there is not enough now obtainable to show its composition except by qualitative tests.

Fetid Gas.—Upon breaking some of the cyrtolite, while at the mine, a fetid odour, quite different from H₂S, was noticed. Simply rubbing two massive specimens together is sufficient to develop this very disagreeable smell.

In conclusion, we take this opportunity to thank Mr. Barringer for his kind attentions and generous services extended to Mr. Niven and to one of us while visiting this very interesting locality.

VANADIUM IN CAUSTIC POTASH.*

By EDGAR F. SMITH.

THE occurrence of vanadium in commercial caustic soda has been noticed (see Baumgarten, *Zeitschrift für Chemie*, 1865, 605, and Donath, *Zeitschrift für Analyt. Chemie*, xxi., 45). As far as I am aware, it has not been observed in caustic potash, hence the following lines.

While engaged in making certain decompositions, for which I employed the ordinary stick potash, I was rather surprised, after saturating the alkaline solutions with hydrogen sulphide, acidulating with hydrochloric acid, and heating for several hours, to discover that the separated sulphur showed a decidedly chocolate-brown colour. This occurred repeatedly. The quantity of dark material was never very great, yet it was present even in potash from alcohol. Some preliminary experiments were made which pointed to vanadium. I therefore

* Read at the Chemical Section of the Franklin Institute, Nov. 19, 1889.

saturated the warm aqueous solution of three pounds of stick potash with hydrogen sulphide. Heat was applied for several hours longer, and during this period the liquid gradually assumed a yellow to deep red colour. Hydrochloric acid was added to distinct acid reaction. The separated sulphur was quite dark in colour. After filtration and washing, the residue was dried and treated with carbon disulphide to extract the free sulphur. The chocolate-coloured mass remaining after this treatment dissolved, with exception of a slight quantity, in yellow ammonium sulphide, from which it was re-precipitated by dilute acid. Again washed, treated with carbon disulphide, and carefully ignited, there remained a crystalline mass. With a small quantity of this last product I made the phosphorous bead test—yellow, passing through dark to green when cool. Another special test consisted in dissolving a portion of the ignited residue in a drop of concentrated sulphuric acid free from iron. One c.c. of water was next added, and to this colourless solution from one to three drops of a dilute potassium ferrocyanide solution, whereupon the liquid acquired a fine green colouration. This latter test Dr. Walz (*American Chemist*, vol. vi., p. 453) employed in detecting the minute quantities of vanadium in American magnetites. He considers it conclusive evidence of the presence of vanadium. The most important test, and that which I applied to the remainder of the ignited residue, after effecting its solution in nitric acid, was to add a large piece of ammonium chloride to the ammoniacal solution. The morning following, crystals of ammonium vanadate had separated. These gave the true vanadium bead, and when ignited, moistened with pure strong nitric acid, and evaporated, left the deep red-coloured residue characteristic of vanadium compounds.

The vanadium sulphide, as first obtained, was impure, consequently the reactions were at times masked, and it was only after eliminating some silver and iron that the reactions were unquestionable.

The impure sulphide from the three pounds of caustic potash weighed about one-half grm.

THE CHEMICAL PROBLEMS OF TO-DAY.*

By VICTOR MEYER.

WHEN, a short time ago, I was called upon to speak before you, I gladly and zealously approached the work which such an occasion seemed to call forth. It seemed to me that it would be an effort worthy of this assemblage of scientific men to recall the permanent additions that chemistry has made in our day to the treasure of human knowledge, and to enumerate the problems which seem to lie nearest us in the future.

A science which, as such, is hardly older than the great European revolution, the centennial of which we witnessed a few months ago, and which, in this short time, has caused changes in our spiritual and material life hardly less than those of the political revolution, such a science, I have thought, may, without temerity, boast of its achievements.

And yet the chemist approaches such a task with a certain hesitation, from which the astronomer, the physicist, and the mathematician are free. Has it not been in our own day that the most prominent orator amongst German naturalists, one who astonishes us by the comprehensiveness of his knowledge, has adopted as his own Kant's judgment on chemistry, namely, that "chemistry is a science, but not a science in the highest sense of the word, that is, a knowledge of nature reduced to mathematical mechanics." And this dictum is accepted, not as

a blemish upon our science, but with the fullest and most perfect recognition of the immense achievements which modern chemistry has registered as its own.

But all of the marvellous successes of the atomic theory and of the doctrine of structure, the synthesis of the most complicated organic compounds, the blessings of an enlarged pharmacopœia, the potent revolution in technological processes, the new and systematic methods of production, which have been characterised by an eminent technologist as "the gaining of gold from rubbish"—all this seems trifling to the mind that looks down from its standpoint of mathematical mechanics when compared with the work of a promised Newton of chemistry, who some day will represent chemical reactions in the thought and in the language of mathematical physics.

And if he who looks from a height is justified in the expression that to-day chemistry, in the recognition of ultimate causes, stands yet below astronomy of the time of Kepler and Copernicus, must not the chemist lose courage if he attempts, before an illustrious assemblage, to raise a song of praise to his science, to glorify what she has done, and what in the future she seems chosen to do? If, in spite of this, the attempt be made, it must be with that resignation which rests upon the belief that "we should consider everything, but to aim only at that which is possible."

Though we share, with full conviction, the expectations of a Newtonian period in chemistry, we hardly venture to hope that that period is near, and even the most enlightened representatives of the newer physical chemistry seem but precursors of that distant era.

Perhaps the chemist, immersed in the daily work of his science, fails to take the comprehensive view of one who, from a distant height, looks down upon the same. But those who are surrounded by the whirl of hourly renewed work recognise, all the more clearly, the immense amount that remains still to be achieved before those distant aims can be realised. This epoch, so rich in pathfinders in the department of physics, has rarely directed the highest order of research into the territory of our science, and especially have the more complicated chemical phenomena been avoided.

If, in a period that has witnessed the discoveries of Helmholtz, Robert Mayer, Joule, Clausius, and van't Hoff, the revolutionising progress of knowledge has been limited to Physics, and if only modest applications of what was gained have been made in related studies, then the epoch seems not yet to be at hand in which chemical processes can be thought of as we think of the movements which we feel as sound, light, or heat.

A humiliating statement! But, strange to say, the chemist of to-day has hardly time to complain of this resignation imposed upon him, and this for reasons easily understood.

If—without question—it is the aim of all natural science to understand phenomena so fully that they may be described in a mathematical form, and, as far as they are unknown, may be predicted, a science which is so far distant from this aim as to look merely for the *path* that shall some day lead to it must be considered as in its infancy. In the present stage our way of thinking and acting has this peculiarity. In every science phantasy must stand as another power alongside of knowledge and reasoning. But the influence of phantasy upon knowledge is all the greater the further this latter is distant from the mentioned ideal. And thus it happens that in the chemistry of to-day phantasy and intuition have a larger scope than in other sciences, and that occupation with the same, besides the pure scientific satisfaction that it yields, brings an enjoyment which, in a certain sense, reminds one of the activity of an artist. He, however, who only knows chemistry as a tradition of perfectly clear facts, or who thinks to see the real soul of chemical study in measuring the *physical* phenomena which accompany chemical transformations, feels no breath of this enjoyment.

* An Address delivered at Heidelberg at the First General Session of the Sixty-Second Meeting of the Association of German Naturalists and Physicians, Sept. 18, 1889. Translated, by L. H. Friedberg, from the *Deutsche Rundschau*, Nov., 1889.

The feeling is only disclosed to him who ventures into that ocean of the unknown that is spread out before us in the *organic chemistry* of the day; to him who is not appalled by a wilderness populated with thousands of individuals, of which every one shows a peculiar fully unknown originality, and to him who attempts to become better acquainted with some of them, even if he is at a loss for a means of approaching them. To proceed with success in this direction is only granted to the genius—the method that leads onward cannot be learned, and it has only been practised with success by a small number of chosen ones.

Indeed, in the experimental study of organic chemistry the "presentiment" of happenings, the actuality of which is not indicated by any law to be expressed in words, has shown surprising results; here the thought is aided by a something which we may meanwhile term "chemical feeling," a name which will disappear as soon as the progressive approach of chemistry to the mathematical physical basis shall have disclosed its meaning and shall have tabulated it amongst the methods which lead to the recognition of the new. The effect of this peculiar chemical method of study is not here to be dwelt upon in detail. Let it suffice to say that without it the most brilliant discoveries in organic chemistry would not have been made, just as little as a Kekulé would, without it, have been unable, in contradiction of numerous data in chemical literature never before doubted, to affirm the non-existence of isomeric monochlorbenzol and of such bodies as were said to consist of a benzol ring and but one bivalent atom. Those significant hypotheses by means of which the knowledge of aromatic substances has been revealed to us, could not have been made solely upon the ground of exact observation; they required, at the same time, a pronounced chemical instinct. There was no logical reason in declaring the existence of a phenylene oxide as an impossibility, since the ethylene oxide did exist; he who nevertheless ventured to do so, and at the same time ran directly in the face of experience, was surely led by a feeling which the present status of chemistry forbids us to replace by a process of thought.

But to return from the field of organic to that of general chemistry. Before we can arrive at a mathematico-physical treatment of chemical phenomena in general, two fundamental problems must be solved; an hypothesis which allows a control by experiment (even within the same limits which to this day are imposed upon physics in regard to the law of gravitation) must answer these questions:—*What is Chemical Affinity?* and *What is Valency?*

By means of laborious detail-work chemistry tries to approach the solution of these enigmas, but he who pursues chemical methods, who stands in the midst of chemical work—which aims only, as at a far distant task, at the discovery of a sure *path*—still sees such obstacles to be cleared away that he gives up the hope of living to see the new chemical era. He finds satisfaction in the consciousness of having exerted his best abilities in the elucidation of some minor and precursory principles.

If now we begin to consider—within the appointed limits—the most important achievements of chemistry, we cannot, at this place and at this hour of our meeting, be in doubt as to what is to be mentioned in the first place. The hospitable city that shelters us boasts of an advantage which is envied her by every other *Alma Mater*; here chemistry for more than a human lifetime has been represented by Robert Bunsen, of glorious name, and the very days which find us here assembled follow immediately the moment in which this hero of science has retired from his academical occupation. Who does not think, at such an hour, of the great teacher around whom ardent pupils from all parts of the globe were accustomed to congregate. But who, being called upon to-day to speak of the results of chemistry within the walls of Heidelberg, would not before all direct an eye upon that one discovery which

has lifted chemistry beyond terrestrial research, which has enabled her, like astronomy, to search the universe and to dissect the starry heavens, chemically, by the subtle appliances of analysis. If "old Heidelberg" has become a pearl amongst German cities by its history, by its numerous traditions, by the incomparable beauty of its situation—if its university is the ideal of the German academical youth, we may well regard as an immortal leaf in its wreath of honour, along with these glorious titles, the union of those two great men who first met in this city in the most courageous enterprise of the penetrating mind; who have pursued with astonishing success the investigation which has made spectral analysis the most potent of scientific weapons, and has rendered their names a charm, calling forth the admiration of the older minds and kindling in the minds of mere school-boys the flame of enthusiasm in the study and exploration of nature. The immeasurable results of that discovery—the consequences of which extend every day over new territories—are known in the widest circles, and to mention them to-day in detail would be but carrying owls to Athens. It behoves us in this place to mention reverently the names of Bunsen and Kirchhoff, to think of them with gratitude, and to hope that men, their equals, may not be entirely wanting in the next generation! The younger one of them, whose scientific fertility was only equalled by his greatness of soul and the charming modesty of his heart, has been taken away from us before old age had naturally limited him. Bunsen we still rejoice to call ours, who now, allowing the tools of his work to drop from his hand, looks forth to the evening of his life in quiet, happy leisure. May he be permitted for a long time to look back upon a life filled with greatest scientific achievements; may his calm friendly eye rest for many years upon the incomparable picture of his beloved Heidelberg.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1889.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MESSRS. W. F. Butcher, C. F. Baker, A. L. MacLeroy, and F. Quincke were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edward Whitley Allsom, Palace View, Cork; William Winsor Haldane Gee, B.Sc., 124, Raby Street, Moss Lane East, Manchester; Arthur Hutchinson, Christ's College, Cambridge; Arthur Hotham McConnell, 10/2; Russell Chambers, Bury Street, W.C.; William Samuel Newman, Madras, India; Saville Shaw, Durham College of Science, Newcastle; William Charles Sayers, 63, High Street, Lewisham, S.E.

The following papers were read:—

106. "*Frangulin*." By Professor T. E. THORPE, F.R.S., and H. H. ROBINSON, M.A.

The authors prepared the glucoside frangulin from the bark of the alder buckthorn (*Rhamnus frangula*) by first extracting with low boiling petroleum to remove plant fat, and next with methylated spirit, which removed the frangulin together with resins, &c. To this extract lead acetate was added to precipitate tannins, and after removing the excess of lead in the filtrate by means of sulphuretted hydrogen, the frangulin was obtained from it. 14 lbs. of the bark gave about 5½ grms. of frangulin.

Seven analyses were made of four different portions of frangulin which had been purified by different methods, and the results agreed with one another and corresponded

to the formula $C_{22}H_{22}O_9$: for every analysis the frangulin was dried at 120° until constant.

The frangulin was hydrolysed and the yellow product insoluble in water was analysed, in two cases after crystallising from alcohol and drying at 120° until constant, and in two cases after crystallising from benzene and drying at 180° . The results corresponded to the formula $C_{15}H_{10}O_5$. The product was directly compared with some emodin from rhubarb, and was found to give the same colour reactions, and the authors are satisfied as to its identity with that substance.

A phenylhydrazine derivative of the product soluble in water, and which has the power of reducing Fehling's solution, was prepared and compared with that obtained from glucose, and was found to possess quite different properties: hence it is concluded that the soluble product of the hydrolysis is not glucose.

The investigation of the nature of this soluble product, and of the equation representing the hydrolysis, will be continued by one of the authors.

107. "Arabinon, the Saccharon of Arabinose." By C. O. SULLIVAN, F.R.S.

In a former communication (*Chem. Soc. Trans.*, 1884, p. 55), under the name of α -arabinose, the author has described a substance obtained by hydrolysis of arabic acid, having an optical activity "well above $[\alpha]_D = 140$ "; this is more fully considered in the present communication. The details of its preparation from geddic acid, an acid obtained from Gedda gum—which the author will describe in a future notice—are fully given. As yet it has not been obtained in a crystalline state: when dried over sulphuric acid in vacuo, and then at a temperature gradually increasing to $75-80^\circ$, it is obtained as a glassy mass, which when pulverised forms a white hygroscopic powder. It has a specific rotatory power of $[\alpha]_D = 198.8^\circ$; and 100 parts have the same cupric reducing-power as 58.8 parts of dextrose. It yields arabinose on hydrolysis, and appears to bear a similar relation to this carbohydrate that saccharon (cane-sugar) bears to glucose: the author therefore terms it *arabinon*, preferring the vowel system of nomenclature to that proposed by Scheibler. Combustions were simultaneously made of saccharon and arabinon with the following results:—

	Saccharon.	Arabinon.	Theory for $C_{10}H_{18}O_9$.
Carbon ..	42.11	42.46	42.58
Hydrogen ..	6.61	6.55	6.38

The molecular weight found by Raoult's method was 239.2; that of a carbohydrate of the formula $C_{10}H_{18}O_9$ is 282, and although the number obtained is low, bearing in mind the fact that this is the case with the "on" carbohydrates, and that the preparation may not have been free from ash constituents, there can be no doubt that the compound belongs to the "on" and not to the "in" or dextrin class. The amount of arabinose obtained on hydrolysing 100 parts arabinon was 104.9; the theoretical yield, if $C_{10}H_{18}O_9 + H_2O = 2C_5H_{10}O_5$, is 106.3.

108. "On the Identity of Cerebrose and Galactose." By HOFACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D.

The authors give the results of an examination of a sample of *cerebrose* prepared from phrenosin, which was placed in their hands early in 1888 by Dr. Thudichum, who first isolated and crystallised this substance. They show that its specific rotatory power, cupric reducing power, and molecular weight, as determined by Raoult's method, are identical with those of *galactose*, thus confirming the recent work of Thierfelder (*Zeit. Physiol. Chem.*, xiv., 209), who has proved the sugar produced by the action of acid on cerebrin to be galactose.

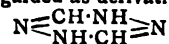
DISCUSSION.

Dr. THUDICHUM said that the specimen of *cerebrose* which has been examined by the author was prepared by him from *phrenosin*, $C_{41}H_{79}NO_8$. Messrs. Brown and Morris's experiments had been conducted in July, 1888,

and Mr. Brown's communication to him (Dr. Thudichum) on the subject, which he held in his hand, was dated August, 1888. Phrenosin consisted of the sugar now shown to be identical with galactose, $C_6H_{12}O_6$; of *neurostearic acid*, $C_{18}H_{36}O_2$, an isomer of stearic acid, fusing at 84° ; and of *sphingosin*, an alkaloid of the formula $C_{17}H_{35}NO_2$. There were, however, present in the brain a number of glucosides or saccharides, of which phrenosin was the most abundant and most characteristic; amongst the more neutral bodies of this kind was *kerasin*, $C_{42}H_{85}NO_8$, and amongst the more acid ones, which formed insoluble compounds with baryta or lead oxide, were three—*cerebrinic acid*, *sphero-cerebrinic acid*, and the principal (in quantity) *cerebrinacid*—compounds containing from 54 to 59 atoms of carbon, and from 9 to 21 atoms of oxygen. Of these, *cerebrinic acid* had also yielded the sugar; the others had not yet been tested in that respect. The compounds of this group present in the human brain were very numerous, and one of them contained as much as 4 per cent of sulphur in organic combination. Some human brains contained as much as 4 per cent of phrenosin, and therefore a human brain of 1500 grms. in weight contained potentially 15 grms. of galactose. In some diseases of a neurotic type he had found "*cerebrose*" in the urine, and of the cases of glycosuria of nervous origin (so-called) a certain proportion was no doubt due to the decomposition of some phrenosin in the brain and the consequent passage of the "*cerebrose*" into the circulation and out of it by way of the renal emanatories. It was an important fact that the crystallised sugar from phrenosin was always accompanied by an almost equal weight of uncrystallisable sugar of which the nature was not yet ascertained. Mr. Brown believed that his (Dr. Thudichum's) crystallised galactose, made from pure phrenosin, contained a little dextrose: the question then arose whether the uncrystallised sugar obtained was altered galactose or dextrose, or a sugar *sui generis*; if it was dextrose, or a sugar *sui generis*, the formula of phrenosin would have to be doubled, and it must be assumed to contain an *amylonide radicle*, such as he in his theory of the organoplastic substances had considered as forming the chemical skeleton of the albuminous matters. The special details concerning the substance alluded to were to be found in his "Treatise on the Chemical Constitution of the Brain," London, 1884, and an exhaustive critical consideration of the literature and chemistry of the "*cerebrosides*" or cerebrin bodies of the brain was contained in his German work on "Anatomical and Clinical Chemistry," Berlin, 1886.

109. "The Action of Chloroform and Alcoholic Potash on Hydrazines." Part III. By S. RUHEMANN, Ph.D., M.A.

The products formed by the interaction of these substances are to be regarded as derivatives of *tetrazine*,—



(*Chem. Soc. Chem.*, 1889, 242). The author describes the di-paratolyl, orthotolyl, and pseudocumyl derivatives, and their behaviour with nitric acid and bromine.

Paraditolyltetrazine is a weaker base than the diphenyl homologue; it forms an unstable monochlorhydride and a monomethiodide.

The ortho-compound appears to be somewhat more basic. It is noteworthy that while the formation of tetrazines from phenyl- and paratolyl-hydrazine is accompanied by that of the formylhydrazine, the formyl-derivative is not produced in the case of orthotolyl-hydrazine, although it is easily obtained by the interaction of the hydrazine and formamide.

Incidentally, the author describes pseudocumylhydrazine and several of its derivatives.

Mr. P. Braham exhibited a spectroscope without a lens, which was described at the meeting of the British Association at Newcastle. It consists of a taper tube, with a slit at one end and a direct vision prism at the other.

NOTICES OF BOOKS.

The British Journal Photographic Almanac and Photographer's Daily Companion, 1890. Edited by J. TRAILL TAYLOR. London: Greenwood and Co.

THE present rage for photography is something altogether exceptional. If we glance into the window of an optician, or a manufacturer of "philosophical" apparatus—as it is still occasionally called—we may be sure to see ten cameras to one microscope, or telescope, or spectroscope.

The volume before us gives the names and addresses of about 125 photographic societies in Britain alone; we can find no estimate of the number of members—amateur and professional—which must certainly amount to several thousands.

But before we pronounce this an encouraging feature we must ask how many of this multitude bestow any portion of their time and their energies on the important applications of photography in astronomy, biology, or geology? We fear that the majority of the host do little more than take portraits. On carefully examining the table of contents we find nothing on microscopic photography. There is, indeed, a paper on "telescopic photography," but it is merely terrestrial telescoping, and gives us nothing which might not be obtained without the telescope, if the operator conveyed his camera nearer to the objects.

Prof. C. Piazzzi Smyth contributes, however, a very interesting paper on photography applied to the violet portion of the solar spectrum; when to the sight and to the author's spectroscopes all was darkness, the camera recognised "spectral lines of inconceivable delicacy, and in appalling numbers."

There still seems to be a little soreness between amateurs and professionals. A writer, speaking on behalf of the former class, reminds us of a time when the professional was not, and when the art was elaborated by amateurs, who had to devise their own apparatus, prepare their own chemicals, and elaborate the method of their use.

One writer here projects to form a photographic Trade's Union, with all the machinery for strikes, and for boycotting refractory members, &c. A "trade union organiser" is to be employed at £2 weekly. The union proposes to place men of equal merit on an equal footing. Here it differs from the generality of trades' unions, which seek to place men of unequal merit on an equal footing. This seems to us the first attempt to extend to brain-workers the benefits—real or imaginary—which result from such combinations.

A writer, who was on board H.M.S. *Thames* during the review at Spithead in honour of the German Emperor, reports that he obtained a negative not merely of two vessels which he intended to take, but also of three others at a considerable distance on the opposite side!

A Forecast of the Religion of the Future: being short Essays on some Important Questions in Religious Philosophy. By W. W. CLARK. London: Trübner and Co.

THIS book was published as far back as 1879, and is said to have been written between 1870 and 1876. Its subject-matter is not of a kind which admits of any formal discussion in the CHEMICAL NEWS. The origin of "Evil," one of the questions here raised, is not one with which scientific men are ordinarily occupied. They prefer to study the ætiology not of evil in the abstract, but of particular evils, such as pathogenic germs, malaria, vermin, blights, and the like, with a view to their destruction.

Mr. Clarke's position is fully antagonistic to doctrinal religion—a matter upon which we do not feel authorised to enlarge. But he is, perhaps, no less at issue with the conclusions of modern science, and with the scientific habit of thought. He seems disposed to recognise the obsolete notions of a fundamental abrupt boundary be-

tween the plant and the animal and between the animal and man. He quotes approvingly from a "recent writer"—not named—that "all progress is preceded by calamity, that all improvement is based upon defect." Of course, if there were no imperfection no improvement would be possible. Equally, of course, if we look back far enough from any of the great epoch-making discoveries in the world's history, we may feel certain of finding some calamity; but here the *post hoc* is not necessarily the *propter hoc*. It seems to us that the greatest improvements are made in times of peace and tranquillity. Shakspeare and Bacon were the offsprings of an age of remarkable national prosperity. Buffon, Lamarck, Lavoisier, and, in our own country, Cavendish, Davy, and Dalton, were not the children of the Revolution. The "Origin of Species" saw the light at a time disturbed neither by war nor by "reforms."

But we cannot undertake to examine in detail theories which have certainly no direct bearing upon chemistry or physics.

Catalogue of Standard Second-Hand and New Books, English and Foreign, on Chemistry and the Allied Sciences, Technology, Physical and Electrical Science, Metallurgy, Agriculture, Brewing, Dyeing, &c. By W. F. CLAY, 2, Teviot Place, Edinburgh.

THIS periodical catalogue has now reached its 28th issue, and certainly does not decline in value. In addition to standard works of quite recent date, we find many scarce and curious books which are otherwise difficult to meet with. The managers of scientific institutions, libraries, &c., will be able to procure from Mr. Clay sets of various journals, transactions, &c., which are now rarely in the market. How such works as the new edition of Watts' "Dictionary of Chemistry" can be offered at such relatively low prices is a mystery.

CORRESPONDENCE.

TO DETECT IRON IN ORGANIC TISSUES.

To the Editor of the Chemical News.

SIR,—I observe that Professor Zorner has recently published a simple method for the detection of iron in the tissues and direct products of plants and animals. His method I understand is merely to allow the organic substance to remain immersed for some time in a fresh solution of ammonium sulphide, when the presence of iron (?) is shown by the surfaces of the tissue in contact with the solution becoming black. The following mode, however, of identifying this metal in organic compounds is certainly more rapid, and I think also more correct and delicate than Zorner's. Heat the substance for a very short time with a little moderately strong pure nitric acid: then add water and potassium sulphocyanide solution. The red stain which forms on the surface of the body and the red colouration which spreads through the solution are of course excellent indications of the presence of iron. Or the substance after treatment with nitric acid and water may be brought into contact with excess of potassium ferrocyanide, and the presence of the metal proved by the formation of a blue stain on the body.—I am, &c.,

ALEXANDER JOHNSTONE.

Edinburgh University.

ELECTRICITY IN CHEMICAL MANIPULATIONS.

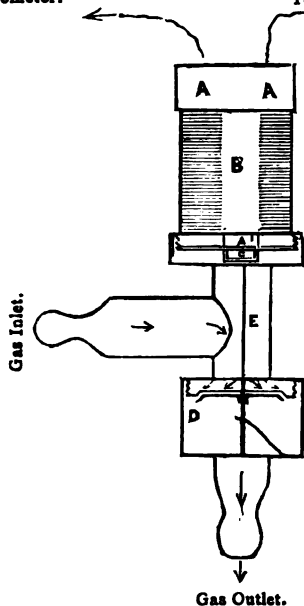
To the Editor of the Chemical News.

SIR,—We observed in the CHEMICAL NEWS, vol. lxi., p. 4, a description by Mr. Reginald Fessenden of a piece of electro-thermostatic apparatus. We do not wish to discount Mr. Fessenden's claims to originality, but we think

it necessary to state that we devised a similar arrangement during the year 1888, and that for the last six months our thermostat has been on the market. We send a rough drawing of the latest form, which has, we think, this advantage over Mr. Fessenden's—that it cannot be tampered with or get out of order. A, A, A' are the iron poles of the electro-magnet, B, which is connected with an electric thermometer in the usual manner by means of a platinum wire fused into the bulb and another thrust down the stem. This is quite sensitive enough for ordinary work. C is the armature which, when the current passes, is pulled against A', pulling with it the rod E and the cup-edged valve, D, which fits accurately into its seat

To Thermometer.

To Thermometer.



and stops all supply of gas which passes round it in all directions when no current is flowing. The necessary quantity of bye flame is, of course easily arranged for. We may say that we lately saw in Paris another form of electro-thermostat, in which a hinged armature was made to act as a clip upon a piece of india-rubber tubing. In our form the valve falls of its own gravity, since we consider that any introduction of springs merely serves to make mechanism more costly, more cumbersome, and more likely to get out of order.

Thanking you in anticipation for the insertion of our letter, we are, &c.,

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 26, December 23, 1889.

Formation-heat of Potas- and Sod-ammonium.—M. Joannis.—For potassammonium, proceeding from solid potassium and liquid ammonia, the result obtained is +1.9 cal.; for sodammonium, with the same conditions, +0.8 cal.

On β -Inosite.—M. Maquenne.—This compound corresponds to the same formula as normal inosite,

$C_6H_{12}O_6$. It also possesses the function of a hexatomic alcohol.

A New Class of Diacetones.—A. Béhal and V. Auger.—This paper is not adapted for useful abridgment.

Analysis of the Meteorite of Mighei (Russia); Presence of a Combination not hitherto met with in Meteorites.—M. Stanislas.—The portion of this meteorite soluble in hydrochloric acid (85.167 per cent of the whole) consists of silica, magnesia, and ferrous oxide. The portion insoluble in acid (14.833 per cent) contains 31.804 per cent of organic matter. The fixed residue is composed of silica, magnesia, ferrous oxide, lime, alumina, with traces of manganic and chromic oxides. The organic matter, which forms 4.72 per cent of the whole, is split up, if heated to redness in a current of hydrogen, into carbon and a volatile compound of a bituminous odour.

Moniteur Scientifique, Quasneville.

November, 1889.

The Origin of Petroleum.—M. Anderson.—A discourse delivered at the last meeting of the British Association.

Detection of Margarine in Butters.—F. Jean.—The oleorefractometer of Amagat and Jean may be used for the detection of margarine. The zero of the graduation of the apparatus is found by means of an oil taken as type, operating at 45°. If the fatty matter of pure cow-butter is then introduced into the interior cell of the apparatus we see a deviation of 35° to the left of the zero of the scale, whilst oleomargarine prepared with the kidney-fat of calves and oxen, examined at the same temperature and under the same conditions, gives a deviation of -19°, or a difference of 16° from pure butter.

Industrial Society of Mulhouse.—Session of September 11, 1889.—M. Prud'homme sent in an extensive memoir on the salts and oxides of chromium. The green gelatinous chromium oxide precipitated from its alkaline solution is not anhydrous. Its composition, when dried at 100°, is $Cr_2O_3 + 5H_2O$. The violet and green salts of chromium oxide do not correspond to two different modifications of this oxide, but their nature depends on the temperature at which the oxide was dissolved. The minimum temperature of the formation of the green salts or of the transformation of the violet salts into green is 65°. Chromic oxide has the curious property of carrying with it, in its alkaline solutions, other metallic oxides, such as ferric and cupric oxides. The alkaline solution of chromic and cupric oxides in blue; if heated to a boil it deposits a red precipitate of cuprous oxide. Chromium chlorate is a very energetic oxidising agent, and may be used with advantage in rendering aniline blacks ungreenable. A solution of double chromium and ammonium sulphite obtained by mixing 45 grms. $K_2Cr_2O_7$, 20 grms. sodium carbonate, 100 c.c. ammonium sulphite at 36° (B.?), 100 c.c. of ammonia, and 1 litre of water keeps well, and may be used for mordanting cloth with chromium oxide, either by a slight steaming or a passage through the Mather and Platt apparatus.

M. Fehr exhibited specimens illustrating his researches on the formation of colouring-matters by the action of light upon a mixture of diazosulphonates and phenols.

M. Bourcart presented a note on the volumetric determination of alcohol and aldehyd by means of chromic acid.

M. Baumann sent a paper on the applications of *negrisine*, a new grey colouring-matter produced by the works of St. Denis (formerly Poirrier).

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. vii., No. 1.

The only chemical matter in this issue is a brief communication by Dr. L. L. de Koninck, referring, with evident scepticism, to the alleged decomposition of cobalt and nickel.

MISCELLANEOUS.

A Curious Invention.—Mr. C. S. S. Webster, F.C.S., sends us an india-rubber stamp which he has devised for stamping the double benzene chain. He is perfectly right in supposing that this little apparatus will be useful to demonstrators, abstractors, and to gentlemen preparing chemical papers for the press, or for reading before any Society. A skilful draughtsman may, indeed, draw such diagrams neatly and easily by hand, but to the majority of chemists we believe that Mr. Webster's little contrivance will be decidedly welcome.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Medical, 8.30.
TUESDAY, 14th.—Institute of Civil Engineers, 8.
 Royal Medical and Chirurgical, 8.30.
 Photographic, 8.
WEDNESDAY, 15th.—Society of Arts, 8. "London Sewage," by Sir Robert Rawlinson, K.C.B. (Adjourned Discussion).
 Meteorological, 7. (Anniversary).
THURSDAY, 16th.—Royal, 4.30.
 Chemical, 8.
FRIDAY, 17th.—Society of Arts, 5. "The India Office Records," by F. C. Danvers.
 Physical, 5. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes. "On Electric Splashes," by Prof. S. P. Thompson. "On Galvanometers," by Prof. W. E. Ayrton, F.R.S., T. Mather, and W. E. Sumpner.

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The Board of Works for the Wandsworth District are prepared to receive Tenders for the supply of CARBOLIC ACID and other Disinfectants for one, two, or three years, at the option of the Board, from the 25th of March next. The Specification and Form of Tender may be obtained at these Offices between the hours of Ten and Four (on Saturday between Ten and Two).

Tenders are to be delivered at these Offices, endorsed "Tender for Disinfectants," on or before Tuesday, the 14th of January inst., and must contain the names and addresses of two responsible persons, to join the Contractor in a Contract for the due execution thereof.

No Tender will be received unless it is made upon one of the printed forms issued from these Offices. The Board do not pledge themselves to accept the lowest or any tender.

By Order of the Board of Works for the Wandsworth District.

HENRY GEORGE HILLS,
 Clerk to the Board.

East Hill, Wandsworth, S.W.,
 January 1, 1890.

BOARD OF WORKS FOR THE ST. SAVIOUR'S DISTRICT.

APPOINTMENT OF GAS EXAMINER.

The Sanitary Committee of the Board will meet on Monday, the 20th instant, at 3 P.M., to receive applications for the appointment of Gas Examiner for the above district, in accordance with Sect. 47 of the Metropolitan Gas Act, 1860, at a salary of £25 per annum. The person appointed must provide, at his own expense, a place suitable for gas-testing within the district, but all necessary apparatus for so doing will be provided by the Board. Applications should be in writing, and accompanied by a copy of testimonials (not more than three in number), and marked outside "Application for Appointment of Gas-Examiner." Six Candidates will be selected and submitted to the Board, who will meet on a subsequent day to make the appointment. Canvassing is strictly prohibited, and will disqualify Candidates. Particulars of the duties may be had on application.

W. H. ATKINS, Clerk.

Offices:—
 Emerson Street, Bankside,
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 January 6, 1890.

BOARD OF WORKS FOR THE ST. SAVIOUR'S DISTRICT.

APPOINTMENT OF ANALYST.—The

Sanitary Committee of the Board will meet on Monday, the 20th instant, at 3 P.M., to receive applications for the appointment of Public Analyst for the above district, in accordance with the provisions of The Sale of Food and Drugs Act, 1875, at a salary of £75 per annum. The minimum number of articles analysed to be 150 annually, and all above that number to be paid for at the rate of 10s. 6d. per sample. Applications should be in writing, and accompanied by a copy of testimonials (not more than three in number), and marked outside "Application for Appointment of Analyst." Six Candidates will be selected and submitted to the Board, who will meet on a subsequent day to make the appointment. Canvassing is strictly prohibited, and will disqualify Candidates. Particulars of the duties may be had on application.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1573.

ON ACETO-METANITROBENZOIC ANHYDRIDE.*

By WILLIAM H. GREENE.

In the reaction of acetyl chloride with silver metanitrobenzoate, L. Liebermann† claimed to have obtained metanitrobenzoyl acetic acid, a reaction which would be inexplicable and without analogy. In the course of another investigation, Bischoff and Rach‡ took the opportunity of studying the action of acetyl chloride on the silver salt of o-nitrobenzoic acid, and found that the reaction did not take place in the sense indicated by L. Liebermann.

Under the name acetylmetanitrobenzoic anhydride, Beilstein in his "Organische Chemie" (ii., 786) describes the product supposed by Liebermann to be metanitrobenzoyl acetic acid, but the properties mentioned accord as little with those which this anhydride should exhibit as with those which would be expected in the acid Liebermann thought he had obtained.

A preparation of this compound, according to the indications of L., by the addition of dry silver metanitrobenzoate to an excess of cold acetyl chloride, and pouring the product into water, yielded an acid fusing between 126° and 137°. 0.1866 gm. of the silver salt of this acid yielded 0.0731 gm. silver.

Ag found, 39.17 per cent. Ag calculated for nitrobenzoate, 39.42 per cent.

The acid is metanitrobenzoic, regenerated from the silver salt employed.

By the reaction of sodium metanitrobenzoate with acetyl chloride, extraction of the product with absolute ether, and evaporation of the latter, aceto-metanitrobenzoic anhydride may be readily obtained, as also by exposing silver metanitrobenzoate to vapour of acetyl chloride and extraction with absolute ether in the same manner. It crystallises in colourless needles, fusible at 45°, and remaining in superfusion at a much lower temperature. It is insoluble in water by which it is not at once decomposed when crystallised, so that it may be washed with dilute sodium carbonate and water, and quickly dried between filter papers without change. The presence of either alcohol or water in the ether used for extraction results in the complete decomposition of all the anhydride.

SIMULTANEOUS DETERMINATION OF CARBON AND SULPHUR IN ORGANIC SUBSTANCES.

By L. PRUNIER.

HAVING been compelled, in researches on a group of sulphuretted organic compounds, to execute numerous determinations of sulphur and carbon, the author has observed that such analyses are not only laborious (if we obey the classical method of making two separate determinations, one for sulphur and one for carbon), but often give erroneous results, generally in deficiency. The larger the proportion of sulphur the more these errors are to be dreaded.

After many trials, he has adopted a process, very manageable and relatively expeditious, which gives in

* Read at the Chemical Section of the Franklin Institute, May 27,

1888 *Berichte*, x., 863.

† *Berichte*, xvii., 2799.

one and the same combustion the determination of the sulphur with more ease and accuracy than at present, and the determination of the carbon, though with rather more trouble and less exactitude.

He employs, to this end, pure crystalline permanganate, which is powdered and mixed with the weighed portion of the substance in question, in the proportion of 80 or 100 parts to 1. The whole is introduced into an ordinary combustion-tube, and the combustion is effected as with copper oxide. It takes place in an atmosphere of oxygen derived from the decomposition of the permanganate, which begins to be given off at 240° or upwards. The gases liberated are allowed to bubble through a solution of permanganate, and the apparatus is terminated by a tube containing baryta-water, which should not become turbid if the process is working regularly. The carbon and the sulphur ought to remain entirely either in the combustion-tube or in the solution of permanganate.

The contents of the tube are extracted with water. All the sulphur is found in the aqueous solution, which is filtered over asbestos to remove a deposit of manganese oxides, sometimes retaining a little carbon.

In half the filtrate, which is previously acidified and decolourised with hydrochloric acid, the sulphur is determined as barium sulphate in the ordinary manner.

The second half of the liquid and the totality of the insoluble residue left upon the asbestos serve for the determination of the carbon, which is rather more troublesome than that of the sulphur. In fact, the carbon is only partially converted into carbonic acid. As M. Berthelot has shown in his researches on the attack of organic substances by permanganate in solution, certain acids, such as the acetic, benzoic, and phthalic, obstinately resist complete oxidation. It is therefore necessary to submit this second half of the liquid to a prolonged ebullition in presence of sulphuric acid after having ascertained that there remains sufficient permanganate to complete the oxidation. All the carbon is thus ultimately transformed into carbonic acid, which escapes and is collected in the ordinary manner.

A similar treatment is applied to the insoluble residue. Lastly, to the quantity of carbonic acid obtained from the insoluble residue there is added double that resulting from the liquid, and from the total the proportion of carbon is inferred.

In the cases when the permanganate used contains substances capable of influencing the determination of the carbon (nitrates, chlorates, &c.), a blank experiment will show the corrections to be made.

This method has been found successful in the analysis of a great number of bodies containing, in some cases, more than 65 per cent of sulphur. Hitherto the determinations have been made on ternary compounds (carbon, hydrogen, and sulphur), or quaternary (carbon, hydrogen, sulphur, and oxygen), but not nitrogenous. Experiment will show if the process is equally applicable to all groups of organic compounds.—*Comptes Rendus*.

THE APPLICATION OF DOUBLE PYROPHOSPHATES FOR THE ELECTROLYTIC SEPARATION AND DETERMINATION OF METALS.

By Dr. ALBANO BRAND.

(Continued from p. 18).

10. *Tin*.—The stannous and stannic pyrophosphates are white and readily soluble in an excess of the precipitant, especially the former. In both the solutions of the sodium and ammonium double salt bear the addition of ammonium carbonate; ammonia occasions precipitation.

The double stannous salt is readily reduced either from a pyrophosphoric or an alkaline solution. On account of

the application of the salt in electro-metallurgy it is to be expected that the deposited metal must be of good quality. In fact, with feeble currents which give up to 0.1 c.c. detonating gas per minute they are dense, adhesive, and of a silvery whiteness, but they become grey if the current is a little stronger.

The quantitative determination of tin by the electrolysis of the double stannous salt is a failure, since a portion becomes oxidised to a stannic salt at the anode and thus escapes reduction. The sensitive reaction for stannous salts (which in a hydrochloric solution give, on the addition of iron chloride and potassium ferricyanide, a precipitate of prussian-blue) can after a time no longer be produced, whilst sulphuretted hydrogen throws down yellow stannic sulphide.

The double stannic salt requires very powerful currents for its reduction. Five freshly-charged Bunsen elements produce no deposit on a platinum capsule if the solution contains 0.3 grm. tin per 100 c.c. By more powerful currents from a dynamo, the metal is obtained as a beautiful dense white deposit of a silky lustre.

The quantitative determination of tin from the double stannic salt did not succeed. In several experiments there was always found a smaller quantity of tin than that corresponding to the quantity of double stannic chloride employed.

It is an open question whether this deficiency results from spitting (in consequence of the liquid becoming heated by the powerful current) or from imperfect reduction, since the completion of the reaction remained doubtful, as sulphuretted hydrogen does not immediately react in the cold with traces of the tin-salt.

This property of tin of not being reduced from the double pyrophosphates, except by powerful currents, might seem to promise a means for its separation from many other metals; but in this case, if the action is prolonged, traces of tin are generally deposited.

A peculiar phenomenon was observed in the deposition of tin. After the white metal has been dissolved away by hydrochloric acid the platinum capsule appears coated with a thin layer intermediate in colour between gold and pinchbeck, and neither soluble in hydrochloric nor in nitric acid. If heated to whiteness this film loses its colour and becomes dull. The weight of the capsule was increased by 0.001—0.002 grm. On melting with salt-petre the film disappears and the weight of the capsule diminishes by some m.grms. In the solution of the melt nothing but platinum can be detected. It is derived from the anode, for with so strong a current a faint odour of chlorine is perceptible even if the solution is not alkaline.

11. *Chromium*.—Chromic oxide forms with sodium and ammonium pyrophosphate double salts, which behave normally in the preparation of the electrolyte. The solutions in ammonium carbonate or ammonia are green or violet. Ammonium sulphide produces no precipitate. On the electrolysis of the double salt the chromic oxide passes into chromic acid, both in acid and alkaline solutions.

If nickel and cobalt is present in alkaline solution along with the double chromic salt, they are deposited quantitatively; but if the alkaline solution contains at the beginning chromic acid, neither nickel nor cobalt is separated, even with a strong current. In presence of iron there appears in the latter case (in a solution mixed with ammonium carbonate) a reddish yellow body on the cathode containing iron and pyrophosphoric acid. If iron occurs in the solution along with chromic oxide, metallic iron is first deposited; but if the oxidation extends to chromic acid the reduction of iron ceases and the above-mentioned body is formed.

12. *Lead*.—The white lead pyrophosphate is soluble in an excess of the precipitant and bears the addition of ammonium carbonate, but it is precipitated by ammonia. The salt precipitated by ammonium pyrophosphate behaves similarly, but it is sparingly soluble in an excess of the precipitant.

From an alkaline solution electrolysis separates simultaneously peroxide on the anode and lead on the cathode; the less of the latter the more alkali is present and the feebler the current. The author has never succeeded in entirely preventing the separation of lead.

From a nitric or a phosphoric solution lead is separated out alone, but the anode is transiently covered with a layer of peroxide. A determination of lead cannot be effected in this manner, as the metal becomes rapidly oxidised in the air.

13. The thallium double salts behave like those of lead and are formed very easily. In a solution of thallium sulphate there appears no precipitate, and dilute acids occasion no precipitation in the solution.

In an alkaline solution the double thallium salt behaves on electrolysis quite like the lead double salt. In a nitric solution metal and sesquioxide are deposited simultaneously, but from a phosphoric, and especially from a sulphuric, solution the thallium is deposited quantitatively (without formation of sesquioxide). There is the same obstacle to the electrolytic determination of thallium as in the case of lead.

14. *Bismuth*.—The white bismuth salt precipitated by sodium or ammonium pyrophosphate is soluble in an excess, and bears the addition of ammonium carbonate, but is precipitated by ammonia.

The double salt in solution is precipitated by dilute acids. This does not contradict the phenomenon that the double salt thrown down from nitric or hydrochloric solutions of bismuth containing little free acid dissolves completely before the acid is neutralised by the alkaline pyrophosphate (which has a basic reaction). In this case there occurs a subsequent deposition in the liquid as long as a trace of free acid is present.

From solutions of the bismuth double salt in an excess of the precipitant bismuth is deposited upon the cathode in an adherent form; but at the same time, white salts separate out on the anode or in acid solutions in the liquid.

A plentiful addition of an alkaline tartrate obviates this evil, but involves another, since the tartaric acid is decomposed in the course of the electrolysis.

On the addition of ammonium carbonate in slight excess the separation of white salt at the anode continues. With a larger excess peroxide apparently makes its appearance, but this deposit does not dissolve in oxalic acid, and hydrochloric acid must be utilised. At the same time, if the excess of ammonium carbonate is very large the metal is more likely to become pulverulent.

These difficulties are obviated by the addition of ammonium oxalate. There is, indeed, a slight formation of yellowish brown peroxide at the anode, but it frequently disappears spontaneously, or it can be easily dissolved by the addition of a drop of oxalic acid towards the end of the process.

For the determination of bismuth the acid solution, slightly diluted, is mixed with four or five times the quantity of sodium pyrophosphate necessary for forming the double salt, and ammonium carbonate is introduced exactly until an alkaline reaction appears, 3–5 grms. of ammonium oxalate (in solution) being finally added.

If much bismuth is present in the solution the salt must not contain too little free acid, as otherwise, on adding the pyrophosphate, the double salt is separated in a curdy form, adhering firmly to the capsule, and cannot be dissolved without difficulty, since heat cannot be applied. Neutralisation with ammonium carbonate before adding ammonium oxalate is essential, since free oxalic acid occasions a pulverulent deposition of the bismuth.

The electrolysis of the double bismuth salt can be effected with a battery of 4–6 Meidinger elements, applying at the outset—according to the strength of the solution, which is diluted to about 200 c.c.—a current of 0.1–1 c.c. detonating gas per minute, increasing it gradually up to 2–3 c.c. towards the end of the reduction. It is thus possible to dissolve as much as 1 grm. bismuth

as double sodium salt per 200 c.c., and to separate it out. It is frequently advisable, in order to obtain an equable deposition over the entire capsule, to apply for a few seconds, at the outset, a more powerful current (1–2 c.c.) per minute until the decomposition is initiated.

As much as 0.25 grm. bismuth can be separated out within twelve hours, beginning with a current of 0.5 c.c. per minute; but it is recommended to use a current of 5 c.c. and more in order to withdraw the last traces. If the proportion of bismuth in the electrolyte is large feeble currents must be used at the beginning. To separate 0.75 grm. bismuth, forty-eight hours were needed. From a solution containing, in 200 c.c., 0.75 grm. bismuth, 0.42 grm. bismuth were thrown down in twenty-four hours by a current of 0.08 c.c. detonating gas per minute.

Towards the end of the electrolysis traces of peroxide are removed, which appear towards the end of the process by a drop of a strong solution of oxalic acid. This must not be done too early, as otherwise the deposition of peroxide may re-commence.

The completion of the reduction is recognised by means of sulphuretted hydrogen. A considerable time is required—four to six hours after the removal of the peroxide—until the last traces of bismuth are reduced and a few c.c. of the electrolyte, after the addition of the reagent, remain clear and colourless as water.

The separated metal gives too high a weight in consequence of oxidation. Hence it is necessary to convert it into oxide, which may be easily effected without loss by dissolving in nitric acid and finally decomposing the nitrate at a red heat.

The form of the anode has an influence on the separation of the metal. If it is a piece of sheet-metal, the coating at the bottom is less dense than at the sides. With an anode of wire the separation is uniform, and the peroxide is easily dissolved by means of a concentrated solution of oxalic acid.

The deposited bismuth has a white-grey colour and a perfectly metallic aspect if feeble currents. With a more powerful current the colour is pale grey or grey, and the metal adheres so firmly that no loss need be feared on washing.

In the course of the previous investigations the author has examined the method of Thomas Moore (CHEMICAL NEWS, vol. liii., p. 209) for the determination of bismuth. He mixes the solution of the metal with tartaric acid, and in order to prevent the deposition of a basic salt, renders it faintly ammoniacal and adds a large excess of vitreous phosphoric acid. The strength of the current for the electrolysis of this solution is stated at for the beginning 20 to 30 c.c. of detonating gas per hour (0.33–0.5 c.c. per minute), and at the end 450 c.c. per hour (7.5 c.c. per minute).

Several experiments have shown that if the solution contain 0.1 grm. of bismuth per 200 c.c. the solution is pulverulent if, on using two (old) Meidinger elements with a current of 0.14 c.c. per minute, a resistance of 80 to 120 ohms is inserted. Even then the metal deposited is not very compact.

15. *Antimony*.—From a solution of antimony terchloride the addition of sodium or ammonium pyrophosphate precipitates a white salt soluble in excess. The solutions bear an addition of ammonium carbonate, but occasion a precipitate. Antimony is thrown down quantitatively by a current of 0.1 to 0.3 c.c. detonating gas per minute, but if the quantities are large it does not adhere firmly enough for accurate determinations.

(To be continued).

A Morphine Reaction.—O. Hesse (*Pharm. Journal and Chemiker Zeitung*).—This reaction was discovered by Kiefer prior to Armitage. Hesse considers that Armitage has not explained the procedure correctly.

AMMONIA-FREE WATER.

By A. G. BLOXAM.

AN analyst who has a considerable practice and is considered no fool by his *clients*, has persuaded me to put on record the possibility of preparing ammonia-free water in any quantity by simply boiling ordinary distilled water in a wide-necked flask; half a gallon of ammonia-free water may be thus obtained in less than an hour. He hopes that other analysts may, by this publication, be spared the tedious process, which he has till now adopted of obtaining such water by distillation.

THE CHEMICAL PROBLEMS OF TO-DAY.*

By VICTOR MEYER.

(Continued from p. 22).

We have mentioned spectral analysis, though it has been almost for an age the common property of science. Let us also cast a grateful retrospect upon a deeply furrowing revolution—of which chemistry also, for several decades, has boasted as a substantial possession—upon the development of the *doctrine of structure*, that solid theoretical foundation from which the proud edifice of modern organic chemistry rises. A generation has grown up around us which has received as a matter of fact this doctrine which still seems new to us older ones. But those far-seeing men, whose eyes recognised the immensely simple in the seemingly impenetrable complication of the carbon compounds, are still actively alive amongst us, and it is their happy lot to reap in their own activity what once they sowed in juvenile work. Here the eye is directed upon the master of chemical research—August Wilhelm von Hofmann; before all upon his researches upon the organic nitrogenous bases—researches which do not find their equal in organic chemistry, and which, even more perfectly than Dumas's fundamental discovery of trichloroacetic acid, allowed the fundamental conception of substitution to expand into the living consciousness of chemists, at first, curiously, by supporting the theory of types in organic compounds and then by promoting the transition to the structural or constitutional view, which at present embraces, with unparalleled perfection, the whole territory of organic compounds.

But the suggestion of this doctrine, which finds its crowning success in the recognition of the inner aggregation of the atoms, is associated for all time with the name of a man who, although a master of rare art in experimenting, knew how to surpass what he had achieved at the laboratory table by the convincing power of his speculative work. We cannot here dispute the part which other eminent chemists have taken in the development of the doctrine of structure—there are, Butlerow, Cooper, Erlenmeyer, Franklin, Kolbe, Odling, Williamson—but the glorious guide in this great and victorious movement forward, he, to whose eyes was disclosed not only the tetravalence of carbon, but also the solution of the problem of the constitution of organic compounds, in the recognition of the property of carbon atoms to be linked to *each other* by their valencies; he is the *philosopher* of organic chemistry—August Kekulé. The name of this discoverer, who also started upon his high and soaring flight from Heidelberg, is justly mentioned *alone* when we want to recall in a word the putting forth and the development of the leading chemical theories.

The researches in this direction are so numerous and so toilsome, and yet the result is so surprisingly simple! The carbon atom is endowed with four, the oxygen atom

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with two, the hydrogen atom with one point of attack for the chemical affinity. The cause of the aggregation of the atoms within the molecule lies in the mutual saturation of these units of affinity or valencies. It is the number of valencies which decides the possibility of the existence of a compound. Amongst the legion of imaginable combinations of these three elements only those are capable of existence in which every valency is saturated by that of another atom. Through this knowledge a new method of inquiry was opened, in particular for organic chemistry, the immense territory of which for many years seemed totally to absorb the working power of chemists. But then dawned the first signs of a further development. Hardly a decade had elapsed since the general admission of the doctrine of valency, when a fundamental deepening of the same was announced, which our science owes to two *savants*, working independently of each other—to Le Bel and Van't Hoff. These chemists, considering those substances which turn the plane of polarisation of light, arrived at views which soon led to a result, until then thought to be out of reach, a conception of the aggregation of the atoms within the molecules in space. Thus a field of study was created which Van't Hoff called "*la chimie dans l'espace*," and which we now call *Stereochemistry*.

It was recognised that the carbon atom stretched out its four valencies in definite directions, and this in a symmetrical manner. The combination of a carbon atom with four other atoms, for example, methane, CH_4 , is representable by the picture of a tetrahedron in the stereometric centre of which the carbon atom is situated, while the hydrogen atoms occupy its four corners.

Numerous cases of isomerism, until then not understood, could be explained in this manner, and were regarded as stereo-chemical ones. The cause of optical activity was found to consist in the presence of an asymmetric carbon atom, that is, one which is combined with four different groups.

Also the stereometric forms of a few simple molecules were considered; it was recognised, e.g., that a compound of three carbon atoms linked together by one bond respectively, could not contain those atoms in a straight line, but that they must lie in the angles of a triangle, the sides of which form an angle equal to that in which the directions of valency of the carbon atom intersect each other.

By the application of these considerations to more complicated molecules, which contain a chain of atoms closed within itself, Adolph von Baeyer has enlarged our theory in a manner full of consequence.

Kekulé, in times past, had recognised that carbon shows a particular disposition to form *closed* chains of six atoms. The discoveries of Baeyer and his followers, as well as Fittig's work on lactones, taught that such closed chains or rings formed of fewer atoms also exist. But while rings of six or five atoms easily form, it is more difficult to combine fewer atoms, four or three, to a closed chain. The cause of this fact Baeyer recognised as lying in the stereometric conditions. The angles which the sides of a regular hexagon and pentagon form with each other very nearly coincide with those in which the directions of the valencies of the carbon atom intersect each other, and thus, in linking five or six atoms together, the circle, so to speak, closes itself, while if more or less atoms are present, this can only be arrived at by strong deviation of the directions of affinity.

But still more surprising discoveries were hidden in Van't Hoff's theory. The gifted Dutch thinker had penetrated to the idea that two atoms which are linked together by a single valency rotate freely around an axis, the direction of which coincides with that of the linking valency, but that this rotation is stopped as soon as double linking takes place. This latter is an immediate consequence of the tetrahedric conception. If I stretch out my forefingers and let their points touch each other, then the hands can rotate around them as an axis; but if

I stretch both thumbs and both forefingers and allow their corresponding points to touch each other, then a system results in which rotation is impossible.

These two propositions of Van't Hoff having remained almost unnoticed for a decade, have lately come into great prominence. In a series of important researches Johannes Wislicenus has proved, that, applying these propositions and at the same time considering the specific affinities of the groups or elements present, the stereometric aggregation of the atoms in certain molecules can be determined with probability. In an ingenious manner he has utilised the addition phenomena shown by carbon atoms trebly linked together for an interpretation of a stereometric aggregation of the atoms in the compounds formed.

Wislicenus, applying Van't Hoff's ideas with courage and strictness, has advanced organic chemistry in an important manner, and has opened a field for experimental research, which heretofore had been avoided with a precaution suggestive of timidity.

New discoveries came from other sides. An intimate research into the oxims of benzil lead to the surprising result, that the validity of the second proposition of Van't Hoff is not without exception. Cases were noticed in which the free rotation of carbon atoms united by a *simple* bond, which Van't Hoff disclosed, did not obtain. Further inquiry into this subject led to a renewal of the question, "What does *chemical valency* really mean?" A question to which the mind incessantly demands an answer. It had long since been suggested that valency had some relation to the electric behaviour of the atoms. The chemistry of the day expresses Faraday's fundamental electrolytic law thus: an electric current which flows through several fused electrolytes, severs in each of them the same number of *valencies*—not of *atoms*.

It was found by von Helmholtz that those quantities of electricity which during the electrolytic process move with the ions, are distributed among the valencies. Riecke, in virtue of his pyroelectric researches, was led to the view that the atoms are surrounded by certain systems of positive and negative electric poles.

Uniting these results with those of purely chemical experimentation, we arrive at the idea that the valencies do not appear as *points* of attack proper, but as having *linear* dimensions. The carbon atom represents itself as a sphere, surrounded by an envelope of ether which contains the valencies. The latter seem to be determined by the presence of two opposite electric poles which rest at the ends of a very short straight line. Such a system is called a *dipole*. The attachment of two valencies to each other consists in the attraction of their opposed poles. It is evident that in a radial position of the dipoles, they form an axis around which the atoms are able to rotate, but that this rotation is upset in case of a tangential position. In what has been said so far, and through further considerations in regard to the electrical charge of the atoms and of the dipoles, a reason is found for the repulsion of the four valencies and consequently for the tetrahedric grouping of the same.

The fact that the valencies can deviate from this position now becomes intelligible; we perceive why the valencies of *one* atom cannot unite with one another, while those of different atoms can combine; it is clear that there can exist two kinds of simple linking, one of which admits of rotation, while the other does not; finally, that in cases of manifold linking the free rotation must be annulled. Hence this hypothesis opens to us an understanding of the most important properties of chemical valency.

So much may be said of the problems relating to the theory of valency.

But the doctrine of substitution has likewise experienced a peculiar enlargement. Dumas first showed that the properties of organic compounds are generally little changed when the hydrogen of the same is replaced by univalent elements or groups. Now it has been learned from later experiments that even much more radical changes in the

composition do not materially influence the properties of the substance. If, for example, we replace in the hydrocarbon *benzol* two carbon and two hydrogen atoms by one atom of sulphur, the resulting product, *thiophen*, resembles *benzol*, chemically and physically, so closely as to be mistaken for it. We learn from this that the sulphur atom is able to take upon itself the functions of four atoms of entirely different nature. Similar facts have been found in regard to oxygen and to the imido group, which is equivalent to it.

Turning away from these researches to cast a glance upon general chemical studies which lie some years behind us, we must, above all, consider one of the most far-reaching discoveries of our epoch, the revelation of the *natural system of the chemical elements*. We owe this to the far-seeing Demetrius Mendeleeff. By the side of the titanic figure of the Russian scholar we see the Englishman, Newlands, and our own countryman, Lothar Meyer, successfully co-operating in the foundation and the structure of this work. What these men created has since become generally known: *they showed that the properties of the elements are functions of their atomic weights*. Mendeleeff taught us to predict the existence and the properties of chemical elements as yet unknown, with a certainty that reminds us of Le Verrier's prediction of the discovery of the planet Neptune. We can say with accuracy that even to-day numerous elements, the qualities of which, as well as the place which they will occupy in the system, can be minutely foretold, wait merely to be discovered.

The natural system has imposed upon us a problem of the greatest significance in the new determination of the atomic weights, the numerical values of which are now of increased interest. But numerous other problems are presented by the new system of the elements. Above all, we are at a loss to discern the cause of the inner nexus of the elements as the system offers it. Also by diligent work the less studied elements must be properly brought within the system. Fortunate circumstances may allow us to discover the numerous elements indicated by the periodic law. Here let us note a peculiar coincidence. We know to-day about seventy elements, but Mendeleeff's table indicates so far two small periods of seven elements each and five large ones of seventeen elements respectively. To these must be added hydrogen forming a "group" in itself.

By addition of these figures, $2 \times 7 + 5 \times 17 + 1$ we obtain exactly the number 100.

It is true that no one can say whether the missing elements will really be discovered or if further new periods might not be indicated by which this number, 100, would be exceeded. But, as far as positive data are at hand, they indicate exactly the number mentioned and nothing points beyond it. An odd coincidence which seems to ally the number of the existing elements with the number of our fingers.

(To be continued).

THE RELATIVE ABUNDANCE OF THE CHEMICAL ELEMENTS.*

By FRANK WIGGLESWORTH CLARKE.

In the crust of the earth, with its liquid and gaseous envelopes, about seventy chemical elements are at present recognised. Others, as yet unknown, are indicated by gaps in the periodic system, and will probably be discovered in the future. Some of the elements are quite plentiful, some are exceedingly rare, and in any thorough discussion of their nature and relations this comparative abundance or scarcity should be taken into account. Even though the full meaning of the facts may not be dis-

coverable for many years to come, it is worth while to put them into something like systematic order.

In its larger aspects the general problem is at present unsolvable, for the reason that we know nothing of the earth's interior. Its surface only is within our certain reach, and from the composition of that we must draw nearly all our conclusions. For that which lies below the crust we must be content with inferences based upon the scantiest of data. Of the crust itself the average composition is easily computable, and the calculation gives results which are in some respects surprising.

In order to have a definite mass of matter under consideration, we may assume for the earth's *known* crust a thickness of ten miles below sea-level. The volume of that crust, including the mean elevation of the continents above the sea, is 1,935,000,000 cubic miles. Of this amount 302,000,000 cubic miles are ocean and 1,633,000,000 are solid matter. The mass of the atmosphere is equivalent to that of 1,268,000 cubic miles of water, the unit of density. For these data, which cover all the terrestrial matter accessible to us, I am indebted to Mr. R. S. Woodward, of the U.S. Geological Survey, and from them the relative masses of solid crust, ocean, and atmosphere can be determined within narrow limits of uncertainty. To sea-water we may assign a density of 1.03, which is a trifle too high, and to the solid rocks a specific gravity not lower in average than 2.5, nor much higher than 2.7. With these values we can get the following expression for the percentage composition of the known matter of the globe:—

Per cent.	Density of crust, 2.5.	Density of crust, 2.7.
Atmosphere	0.03	0.03
Ocean	7.08	6.58
Solid crust	92.89	93.39
	100.00	100.00

In short, we may regard the earth's crust, to a depth of ten miles, as composed essentially of 93 per cent solid and 7 per cent liquid matter; treating the atmosphere as a small correction to be applied later. More elaborate estimations are unnecessary. Since the known nitrogen of the earth is mainly in the atmosphere, its relative scarcity as an element is at once curiously manifest. It cannot possibly exceed 25-1000ths of one per cent of the total.

For the composition of the ocean, the data given by Dittmar in the "Reports of the *Challenger Expedition*" are perhaps the best available. The maximum salinity

Composition of Salts.

NaCl	77.76
MgCl ₂	10.88
MgSO ₄	4.74
CaSO ₄	3.60
K ₂ SO ₄	2.46
MgBr ₂	0.22
CaCO ₃	0.34
	100.00

Composition of Ocean.

O	85.79
H	10.67
Cl	2.07
Na	1.14
Mg	0.14
Ca	0.05
K	0.04
S	0.09
Br	0.008
C	0.002
	100.000

* Read before the Philosophical Society of Washington, October 26, 1889.

he puts at 37.37 grms. of salts in the kilogram. of water, and by taking this figure instead of a lower value we can make an allowance for saline masses enclosed in the solid crust, which would not otherwise appear in the final averages. Combining this datum with Dittmar's statement of the average composition of the ocean salts, we get the second of the subjoined columns. The traces of other elements, not named here, which have been found by various observers in sea-water, are too small to be considered.

Dissolved gases need not be taken into account, and no other constituent of the ocean can reach 0.001 of one per cent.

In the case of the solid crust of the earth the problem of ascertaining its mean composition is far less simple; for the crust is not an homogeneous body, but is made up, so to speak, of shreds and patches; of old crystalline rocks, of volcanic outflows, and of all manner of deposits of sedimentary origin. It is veined and seamed with diverse minerals, it encloses pockets of various materials, and upon its surface are quantities of organic matter and great bodies of fresh water. At first sight it would seem to be impossible to determine the average composition of such a mass, and yet, upon consideration, the question is not seriously complicated. In a crust ten miles thick a section having the superficial area of the United States represents only about 1.5 per cent of the total; so that all veins, pockets, patches, organic substances, &c., become insignificant in comparison with the whole mass, and even the lakes and rivers are neglectable quantities. On any attempt to compute their percentages they vanish into the dim recesses of the remoter decimals. Discarding these trivial constituents the question becomes one of the mean composition of the dominant rock material, and in that form it is comparatively simple.

In the first place we may assume that the volcanic and crystalline rocks represent pretty closely the general composition of the whole crust; for from them the sedimentary rocks have been formed, and the latter differ from the parent formations only in the carbon which they have taken up from the air and in the loss of saline constituents which have been leached out to the ocean. For this gain and loss, respectively, approximate corrections are possible.

In the second place, we must regard the original rock matter, volcanic and crystalline, as being, in a large sense, fairly homogeneous. However greatly these formations may vary locally, they should average pretty much alike all over the world when sufficiently large areas are considered. This assumption can be tested in the light of evidence as follows:—We may average together great numbers of analyses, grouped in various ways, and so determine whether the results are sensibly constant. This has been done in the subjoined table, minor and occasional constituents being temporarily omitted, to be separately considered later.

A. The mean of 82 analyses of organic rocks from the Western Territories of the United States, published in Clarence King's Survey of the Fortieth Parallel.

B. 64 analyses of rocks from the Yellowstone Park, taken from the laboratory records of the U.S. Geological Survey.

C. 54 analyses of volcanic rocks collected in Northern California, also from the Survey records.

D. 39 analyses of eruptive rocks from various localities in the Western United States, taken from the Survey records.

E. 80 crystalline and archæan rocks from all parts of the United States. Of these analyses, 50 were taken from the Survey records, 23 from the 40th Parallel Report, and 7 from the "Report of the New Hampshire Survey," vol. iii.

F. 75 analyses of European volcanic and crystalline rocks, taken at random from five recent volumes of the *Neues Jahrbuch*.

G. 486 miscellaneous plutonic rocks, analysed between

1879 and 1883, and collected by Roth in his "Beiträge zur Petrographie der Plutonischen Gesteine."

H. The mean of the foregoing 880 analyses.

	A.	B.	C.	D.	E.	F.	G.	H.
SiO ₂ ..	61.89	61.89	60.49	60.66	60.50	59.80	56.75	58.59
Al ₂ O ₃ ..	15.71	15.73	16.08	15.46	14.30	14.65	14.90	15.04
Fe ₂ O ₃ ..	1.81	3.18	2.47	2.74	3.35	4.99	4.58	3.94
FeO ..	3.65	2.40	2.86	2.27	4.31	2.92	3.71	3.48
CaO ..	4.51	4.58	6.15	4.71	3.52	5.19	5.79	5.29
MgO ..	2.40	3.08	4.31	3.35	5.00	3.45	5.22	4.49
K ₂ O ..	3.54	2.70	1.80	3.97	2.52	3.06	2.90	2.90
Na ₂ O ..	3.28	3.70	3.31	3.54	2.49	2.98	3.24	3.20
H ₂ O ..	1.69	1.59	1.12	0.97	2.53	2.09	2.12	1.96
	98.48	98.85	98.59	97.67	98.52	99.13	99.21	98.89

That these means are remarkably concordant, especially as regards the columns A to F, is at once evident; but a reduction to elementary form renders the agreement even more striking.

	A.	B.	C.	D.	E.	F.	G.	H.
Si ..	28.88	28.88	28.23	28.31	28.23	27.91	26.50	27.34
Al ..	8.31	8.32	8.51	8.18	7.57	7.75	7.89	7.96
Fe ..	4.11	4.09	3.96	3.68	5.71	5.77	6.09	5.47
Ca ..	3.22	3.27	4.39	3.37	2.51	3.71	4.13	3.78
Mg ..	1.44	1.85	2.58	2.01	3.09	2.07	3.13	2.69
K ..	2.94	2.24	1.49	3.29	2.09	2.54	2.41	2.41
Na ..	2.43	2.74	2.46	2.63	1.85	2.21	2.56	2.37
H ..	0.19	0.18	0.12	0.11	0.28	0.23	0.24	0.22
O ..	46.96	47.28	46.85	46.09	47.28	46.94	46.26	46.65
	98.48	98.85	98.59	97.67	98.52	99.13	99.21	98.89

The thesis that the crust of the earth is fairly homogeneous in composition is thus sustained by positive evidence. The variations in the foregoing table are as small as could be reasonably expected.

So far, however, only nine of the rock-forming elements are accounted for. The proportions of the others are less easily computable, although in some cases fair estimates can be made. In certain directions very many of the analyses considered, especially in the columns A and G, were incomplete, constituents like titanium, manganese, phosphorus, &c., having been ignored as not essential to the purpose of the analyst. These substances appear in part, therefore, as impurities in the silica and alumina, rendering the latter a trifle too high.

For several of the less frequently determined elements the laboratory records of the U. S. Geological Survey furnish data. In 211 analyses of volcanic and crystalline rocks there recorded, titanium, manganese, and phosphorus were determined in a great majority of cases, and other elements appear frequently enough to prove something as to their relative abundance. Taking these 211 analyses all together, they show the following mean percentages for the constituents in question:—

TiO ₂ ..	0.55
P ₂ O ₅ ..	0.22
MnO ..	0.10
CO ₂ ..	0.37
S ..	0.034
Cr ₂ O ₃ ..	0.021
BaO ..	0.033
SrO ..	0.009
Cl ..	0.012
Li ₂ O ..	0.011

All of these figures, obviously, are *under-estimates*, for the determinations were not made in all cases. Furthermore, the rocks analysed were varied enough in origin, locality, and character to avoid any cumulative error due to the peculiarities of any one formation or area. The value for titanate oxide includes whatever zirconia may have been present in the various rock samples, but,

although the latter base is widely diffused, its proportion cannot be very high. Titanium, therefore, must be regarded as more abundant than phosphorus, manganese, or sulphur—a result hardly to have been expected. This conclusion, however, is borne out by evidence from other sources. Titanium is rarely absent from the older rocks; it is almost universally present in soils and clays, and it is often concentrated in great quantities in beds of iron ore. Having no very striking characteristics and but little commercial importance, it is easily overlooked, and so it has a popular reputation for scarcity which it does not deserve. Among all the elements it probably ranks tenth or eleventh in point of absolute abundance, and is rare only as regards obvious concentrations.

For phosphoric acid and manganese the data given are probably not far out of the way, but in the case of carbon the estimation is more troublesome. The percentage of CO_2 in volcanic and crystalline rocks, 0.37, is doubtless untrustworthy, for the reason that surface rocks are mainly represented, in many of which alteration may have begun. The figure, however, may be used as an offset for the undeterminable carbon existing in coal, shales, petroleum, &c. As regards the limestones, rough estimates of their quantity must suffice, and we may provisionally accept that of T. Mellard Reade, as given in his essay on "Chemical Denudation in Relation to Geological Time." According to Reade, the existing bodies of limestone are equivalent to a layer of the rock 528 feet thick and completely enveloping the globe. This is approximately 1 per cent of the crust under consideration, and represents 0.44 per cent of CO_2 . To this we may add the 0.37 per cent given above, making 0.81 per cent in all—an estimate which can hardly be too low.

In the case of sulphur, the figure given, 0.034 per cent, is surely much too low, for sulphur is abundant both in sulphates and in sulphides, and iron pyrites especially is widely diffused. The absolute proportion of this element seems to be hardly determinable. It should be at least 0.05 and probably not over 0.10 per cent. For chlorine, chromium, barium, and strontium, the figures are minima, but cannot be very largely increased. The value for lithia is probably not far out of the way, for that oxide is almost universally present in minute traces in the older crystalline rocks, although it is rarely estimated in ordinary analyses.

Now, taking the mean of 880 analyses as cited in column H of the table, we may insert in it the additional values so far determined, but with certain qualifications. In about half of the analyses TiO_2 , P_2O_5 , and Cr_2O_3 were not estimated, but their amounts appear in the figures for silica and alumina. The silica, then, may be reduced by

about one-fourth the percentage of the titanic oxide, and the alumina by the other fourth, plus half the values assigned to P_2O_5 and Cr_2O_3 . Making these corrections, reducing to elementary form, and re-calculating to 100 per cent, we get a rough approximation to the mean composition of the solid crust of the earth. To this approximation the other unestimated elements may be regarded as future corrections of very small amount. Combining this result with the mean composition of the ocean, and including 0.02 per cent for the nitrogen of the air, we get the final column to illustrate the abundance of the elements so far as at present known. Quantities less than 0.01 per cent are left out of consideration.

Nineteen of the elements are here provided for with very varying degrees of probability, although their order in the last column is presumably correct. The uncertainty may reach one per cent in the cases of silicon and iron, one-half as much with aluminum and oxygen, and is proportionally less for the other elements specified. The remaining elements, more than fifty in number, can hardly aggregate over one per cent altogether, and not one of them could pass 0.05 per cent in relative quantity. Some of them may be briefly considered in detail as follows:—

Fluorine.—Abundant in fluor-spar and apatite and present in many rocks as a constituent of topaz or mica. If the phosphorus in the foregoing estimate, 0.09 per cent, represents mainly apatite, the proportional amount of fluorine would be 0.02 to 0.03, the minimum assignable value.

Glucinum.—Widely distributed as beryl and easily overlooked in small traces. If determined, it would appear as a correction to the alumina.

Boron.—Comparatively abundant in tourmaline and datolite, and conspicuous in certain volcanic waters; difficult to estimate.

The Cerium Group.—According to Cross and Iddings, allanite is a wide-spread constituent of rocks. The same is true of monazite, as shown by Derby. These elements, together with thorium, zirconium, and the yttrium groups, would appear as corrections to alumina.

Nickel.—Frequent in rocks composed of or derived from olivine. Less than 0.01 per cent.

The Metallic Acids.—stannic, molybdic, tungstic, columbic, and tantallic.—These, if determined, would form corrections to silica. The same is true, to some extent, of barium when present in rocks as sulphate.

The Heavy Metals.—Widely distributed in rocks, according to Sandberger's researches, but very small in quantity.

In the larger items, say from oxygen down to the alkaline metals, the estimates here given do not differ very widely from others which have been long current in chemical and geological literature. They rest, however, upon fuller evidence, and the discussion is, perhaps, more complete. In the smaller items the new results display the greatest novelty, and future modifications are most likely. The comparative rarity of carbon and sulphur is, to say the least, surprising.

On the theoretical side the results attained are not to interpret. That nine of the chemical elements should constitute, at the lowest estimate, 98 per cent of all known terrestrial matter is somewhat startling and difficult to comprehend. Are the other elements concentrated in the interior of our planet? On this point there is little positive evidence.

The mean density of the earth, 5.5 to 5.6, is more than double that of the rocky crust, and the difference may be accounted for as a result of pressure, or by supposing that, as the globe cooled, the heavier elements accumulated towards the centre. Both suppositions may be true in part, but less weight is to be placed upon the second, for the following reason:—A mixture of the elements in equal proportions, in the free state and as they behave at the earth's surface, would have a specific gravity of about

	Solid crust, 93 per cent.	Ocean, 7 per cent.	Mean, including air.
Oxygen ..	47.29	85.79	49.98
Silicon ..	27.21	—	25.30
Aluminum ..	7.81	—	7.26
Iron ..	5.46	—	5.08
Calcium ..	3.77	0.05	3.51
Magnesium ..	2.68	0.14	2.50
Sodium ..	2.36	1.14	2.28
Potassium ..	2.40	0.04	2.23
Hydrogen ..	0.21	10.67	0.94
Titanium ..	0.33	—	0.30
Carbon ..	0.22	0.002	0.21
Chlorine ..	0.01	2.07	0.15
Bromine ..	—	0.008	
Phosphorus ..	0.10	—	0.09
Manganese ..	0.08	—	0.07
Sulphur ..	0.03 +	0.09	0.04 +
Barium ..	0.03	—	0.03
Nitrogen ..	—	—	0.02
Chromium ..	0.01	—	0.01
	100.00	100.000	100.00

73. In combination the density would be greater because of condensation, and below the surface it would also be increased by pressure. Hence it seems clear, since the density of the earth is only 5.5, that in the planet as a whole the lighter elements must very considerably exceed in quantity the heavier ones. Twenty-nine of the known elements have densities below 5.5, and forty exceed that figure, iron being the only one of the heavier group which is at all abundant. The greater part of the earth's mass is almost certainly to be found among the twenty-nine lighter elements. The others may be more plentiful at the centre of the globe than on its surface, but few beside iron can be dominant constituents. This evidence seems to be clear, even though it is not proof positive.

An attempt was made in the course of this investigation to represent the relative abundance of the elements by a curve, taking their atomic weights for one set of ordinates. It was hoped that some sort of periodicity might be evident, but no such regularity appeared. No definite connection with the periodic law seemed to be traceable. And yet certain other regularities are worth noticing. All of the abundant elements are low in the scale of atomic weights, reaching a maximum at 56 in iron. Above 56 the elements are comparatively rare, and only two of them, barium and strontium, appear in my estimates. Below oxygen, hydrogen alone approaches one per cent, while between oxygen and iron only scandium and vanadium are of neglectable rarity. Furthermore, in several elementary groups abundance diminishes with increase of atomic weight. This is plainly seen in the series potassium, rubidium, and caesium; in sulphur, selenium, and tellurium; in chlorine, bromine, and iodine; in arsenic, antimony, bismuth, &c., &c. The regularity is not certainly invariable, but it occurs often enough to be suggestive.

Perhaps a part of the difficulty in tracing relations of this sort arises from the fact that our field of view is limited to the earth, and does not include the whole solar system. Indeed, several writers, reasoning on the broader basis of the nebular hypothesis and noting the low densities of the outer planets, have argued that the latter may contain the lighter elements mainly, while the heavier substances are concentrated at the original nucleus, the sun. Along this line, however, close reasoning is impossible, partly because evidence is lacking, and partly because the conditions of temperature and pressure differ so widely between the sun and the other heavenly bodies. As thus attacked, the problem becomes one of enormous complexity, and even the solar spectrum gives us no conclusive evidence. That oxygen and silicon are not conspicuous in the sun's atmosphere we may admit, but that non-volatile silica is absent from the solar body is by no means certain. We may assume that compounds can exist nowhere in the sun, but the assumption is unprovable. As to the composition of the outer planets we know practically nothing. How far they may differ from each other, from the earth, and from the sun is, as yet, a matter of pure conjecture.

If, despite Mendeleeff's recent demurrer, we assume that the elements have been evolved from one primordial form of matter, their relative abundance becomes suggestive. Starting from the original "protyle," as Crookes has called it, the process of evolution seems to have gone on slowly until oxygen was reached. At that point the process exhibited its maximum energy, and beyond it the elements forming stable oxides were the most rapidly developed, and in the largest amounts. On this supposition the scarcity of the elements above iron becomes somewhat intelligible; but the theory does not account for everything, and is to be regarded as merely tentative. It is legitimate only so long as its purely speculative character is kept clearly in view. If, however, the evolution of the elements is admitted, it is clear that the later stages of the process must have been seriously conditioned by the chemical affinities developed at first.

NOTICES OF BOOKS.

Applications Industrielles des Residues provenant des Piles aux Bichromates ("Industrial Applications of the Residues derived from Bichromate Batteries.") By GEORGES FOURNIER. Paris: Bernard Tignol.

THE author describes certain electric lighting installations in which the energy employed was obtained by means of bichromate batteries. Both worked satisfactorily, but both came to an end in consequence of the failure of the processes for regenerating or for utilising the residues. In one process, proposed by MM. Grenet and Jarriant, the spent liquids were treated with calcium carbonate, which threw down chromic oxide, but also calcium sulphate, and also a quantity of zinc oxide. The resulting mass was treated like a chrome ore, but, unfortunately, the presence of the calcium sulphate so delayed, or even prevented, the necessary reaction that the process failed.

The other method of treatment tried by the Chrome Company, we believe under the direction of the author, worked successfully, but was stopped by the forced liquidation of the Chrome Company, in consequence of the failure of the bank in which their funds were deposited.

The author's process is first to neutralise every trace of acid by means of zinc turnings, which are placed in boxes of perforated wood suspended in the liquid. If the salt employed in the batteries has been potassium dichromate, chrome-alum crystallises out, and is at once saleable. If the sodium salt has been employed, metallic zinc, suspended in the solution previously heated to 100°, throws down the chrome in the state of hydroxide and takes its place. Zinc oxide may also, if convenient, be used for the precipitation of the chrome. The precipitate if well washed may be put to various uses. By a simple ignition it is convertible into chrome green, used in colouring glass, painting on porcelain, and producing fast colours for printing on paper. If combined with boric or phosphoric acid it yields a beautiful emerald green; chrome picrate is an advantageous substitute for the objectionable arsenical greens; with cobalt it yields a splendid turquoise green, and with alumina a grass green. It may also be converted into a basic sulphate, of value in woollen dyeing.

The liquid from which the chrome has been thrown down contains an alkaline sulphate and zinc sulphate. From this liquid the zinc is precipitated by the gradual addition of dilute milk of lime. The supernatant liquid then contains potassium (or sodium) sulphate, whilst the precipitate is a mixture of zinc hydroxide and calcium sulphate. This deposit is well stirred up in water and treated first with zinc sulphate, until the reaction becomes slightly acid, and then with a solution of potassium dichromate, 1 kilo. to 15 litres of water. The yellow precipitate thus obtained is sold as a yellow colour, and, though containing calcium sulphate, is preferable to chrome-yellow (lead chromate), inasmuch as it does not blacken on exposure to impure air.

In an additional chapter, the author gives instructions for obtaining chromic acid from calcium chromate.

It is possible that the process of M. Fournier may give a considerable impulse to the use of the bichromate battery.

The Cosmic Law of Thermal Repulsion. An Essay suggested by the Projection of a Comet's Tail. New York: J. Wiley and Sons.

THE author of this little work withholds his name, and sums up his doctrine in the words, placed as a motto on his title page, that "Thermal repulsion, like gravitational attraction, is universal between masses as well as between molecules of matter." Starting from this principle he arrives at some strange results. Astronomers and

physicists have concluded that the moon is a dead world, where all the liquid and gaseous matter has been gradually withdrawn into its interior. Our author, on the contrary, holds that the moon's atmosphere and ocean have yet to be formed. He writes:—"The moon must gather meteors as rapidly as the earth, in proportion to size, and the hydrogen and other gaseous matter striking the moon is doubtless at once converted into an atmosphere enveloping the solid body. The moon has not yet gathered enough probably to fill the depressions in its surface, where this atmosphere would first accumulate." He continues:—"The moon appears now to be in the condition that the earth was before the formation of stratified rocks. There is no evidence that the earth during that period had an atmosphere: the indications are that it had none, and it is certainly possible that the earth, in the ages after the igneous period, gathered its atmosphere from meteoric and cometary matter."

Here, then, is the admission that the earth had an igneous period, which has now passed away. Yet the author does not recognise that such secular cooling must convert gaseous matter into liquids and ultimately into solids.

Elsewhere, we find it laid down that "nothing can fall into the sun." If this view is correct, the sun's heat cannot be maintained by the fall of meteorites. Surely a system which leads to conclusions such as those which we have quoted must require a very thorough demonstration before it can claim the acceptance of the scientific world.

We may well also be surprised at finding intelligence placed in the category of "forces," along with gravitation!

A Treatise on the Metallurgy of Iron: Containing Outlines of the History of Iron Manufacture, Methods of Assay and Analysis of Iron Ores, Processes of Manufacture of Iron and Steel, &c. By H. BAUERMAN, F.G.S., Associate of the Royal School of Mines, Associate Member of the Institution of Civil Engineers. Sixth Edition, Revised and Enlarged. London: Crosby Lockwood and Son.

The author of this work points out some very important differences between the ores of iron and those of the other metals. A mineral containing iron is worth working only if the proportion of actual metal is very considerable, and further, if no injurious ingredients are present. An ore containing 5 to 10 per cent of copper would be very valuable, whilst the same proportion of iron in an ore would be neglected.

Again, the iron ores vary comparatively little in their composition. Substantially speaking, all of them contain their iron in the state of oxide, and all are reduced by the action of carbon or of carbon monoxide. The ores of the other useful metals may be oxides, sulphides (simple or complex), chlorides, or may even be in the free state, and the methods of smelting and refining are, of course, very varied.

Another peculiarity of iron is here mentioned, viz., that when absolutely pure it is of no commercial value. The other metals, on the contrary, rise in value for most purposes exactly in proportion as they approach a state of chemical purity.

On the other hand, minute traces of alien elements, metals or non-metals, singularly modify the properties of iron, for the better or the worse. Here we have a number of problems, the elucidation of which will be of great practical value, and which will still require prolonged and delicate investigation.

We are glad to find that the use of the spectroscopic in controlling the conversion of charges, according to the Bessemer process, is here fully recognised. It is admitted at the same time that the exact chemical character of the spectrum of the Bessemer flame is not yet accurately determined.

The supplementary notes appended to the present edition, give an account of the increase of size in the Cleveland blast-furnaces, and of the purple ore, or "blue billy," obtained at Widnes from copper pyrites which have been deprived of their sulphur and copper. We cannot help regretting that the name "blue billy" should be thus applied, since it has long been in use for the spent lime from gas-works.

We find further an account of the composition of the gases of the Bessemer converter, paragraphs on the constitution of iron and steel, on manganese steel, on Gjer's soaking-pit, on Mittis iron, and the new Finland direct reductive processes.

The fact that this work has already reached its sixth edition shows that it is fully appreciated by metallurgists.

Year-Book of Pharmacy: Comprising Abstracts of Papers relating to Pharmacy, Materia Medica, and Chemistry Contributed to British and Foreign Journals from July 1st, 1888, to June 30th, 1889. With the Transactions of the British Pharmaceutical Conference, at the 26th Annual Meeting, held at Newcastle-on-Tyne, September, 1889. London: J. and A. Churchill.

THE Presidential Address, here given, deals with a very important subject, the purity of substances used in medicine. The speaker admitted that the fact of "drugs" being included in the "Sale of Food Act" was an indication that purity was not universal. He noted the fact that few pharmacists have obtained the post of Public Analyst, and enquired whether, notwithstanding their acquaintance with pharmacy, they were deficient in chemical and microscopical skill.

Referring to the decline of chemistry in England, referred to by Prof. Tilden at the Bath Meeting of the British Association, the President raised the question whether our shortcomings—at least as regards the manufacture of pharmaceutical products—may not be in part due to the exceptional stringency of our Excise regulations. He recognises that the Board of Inland Revenue has become in some degree convinced of its error, and it must not look back.

Our opinion is, of course, that our relatively unsatisfactory position in chemistry, as well as in other sciences, is mainly due to our examination system of education. Hence, we are pleased to see that Mr. Umney is with us to some extent, as he makes the very temperate admission that "examinations are not an unmixed blessing," and that they are "subject to no inconsiderable abuse." He further adds:—"It is to be feared that if the students of to-day were asked why they studied, that by far the larger portion would be bound to acknowledge that they were only occupied in cramming into themselves, in the most rapid and easy fashion, the minimum amount of information that would help them to pass their examinations."

Among the more important papers read at the Conference was one on the action of soft waters upon lead, and one on poisoning effected by means of vermin killers.

CORRESPONDENCE.

PENDULUM EXPERIMENTS AND GRAVITATION.

To the Editor of the Chemical News.

SIR,—The first paragraph in Mr. J. Baynes Thompson's last letter is perfectly correct, and in this only can I entirely agree with him. It would be impossible, with his apparatus, to detect, much less to measure, the excessively small deviation which gravitation acting alone would cause. It is for this reason that no one else uses a pendu-

lum with so rapid a period of oscillation as that now referred to. If the length were made four times as great, the true deflection, whatever it might be, would be four times as great and the period would be twice as great. If the pendulum were 10,000 times as long, the deflection would be 10,000 times as great and the period $\sqrt{10,000}$, or 100 times as great, and so on. Now, it is evident enough that a pendulum 10,000 times as long, that is, a few miles long, is not practicable, but if the same bob that Mr. Thompson used were hung at the end of a torsion arm with another one to balance it, there would be no difficulty in obtaining such a period, or, in fact, one of five or ten minutes. The deflection, then, of each of the attracted weights, if there were a pair of attracting weights, would be the same as they would be if either of them formed the bob of a pendulum swinging in the same period. In other words, the deflection can easily be made 10,000 times as great as what, in Mr. Thompson's instrument, as he himself says, is far too small to be detected. The true effect of gravitation can thus be observed and measured. As to the difficulty of calculation, it does not exist. The other difficulties of experiment, it is true, have given trouble, but they may be, and have been, entirely overcome. The only reason why Mr. Thompson's pendulum seemed an improvement on the Cavendish apparatus, as usually made, is that it is far too stable to respond to the true effect of gravitation, or to any disturbing causes which may be comparable to the gravitational attraction.

These disturbing causes are apt, unless very specially provided against, to produce effects not only comparable to, but far in excess of, the true effect of gravitation; the large forces observed show that one of these, or possibly more than one, is acting with great success. The fact that there is a steel knife-edge shows that possible magnetic disturbances have not been entirely guarded against, but I am inclined to think that the chief disturbing cause is motion of the air due to excess or defect of temperature between the fixed and hanging weights and the air. It might be worth while to warm them a little purposely.

There were two points in Mr. Thompson's original communication which it seemed hardly necessary to correct, namely, that the force required to deflect a pendulum is not proportional to the versed sine, as he supposes, but to the sine of the deflection. As with small angles one varies as the square of the other, calculations based on the versed sine do not apply. Then, again, it is not usual, in finding the effect of distance, to measure the distance between the surfaces, as Mr. Thompson seems to have done, but, in the case of spheres, to measure the distance between the centres of the heavy bodies, and, in the case of bodies of other shapes, between points near the centres, which can only be found by long and troublesome calculation.

Though either of these would be sufficient to entirely vitiate any conclusions at which Mr. Thompson might have arrived, had the deflections observed been due to gravitation, I did not consider that it was worth while to point them out, since, had no spurious action occurred, no deflection of any kind could have been observed.—I am, &c.,

C. V. BOYS.

GRAVITATION.

To the Editor of the Chemical News.

SIR,—A friend has shown me that most astounding article on "Pendulum Experiments," which appeared in the CHEM. NEWS. (vol. lx., p. 295), in which the author gravely applies the Newtonian law of gravitation for two indefinitely small particles to the case of two massive cylinders of lead, and, because he does not find their attraction to be inversely proportional to the square of the shortest distance between their surfaces, denies the law! It would be a mere waste of time to point

out the childish error involved in such work as this, but I desire to call the attention of your readers to small subtle fallacy usually exhibited by people who write about the bombarding or "pelting" theory of gravitation. The fallacy is this: two bodies, *a* and *b*, in presence of each other in the ether screen each other on their adjacent sides from the pelting of the atom streams, and so experience a pressure towards each other. On the contrary, they do not screen each other at all, for we must remember that by reflection from the surface of *b* there will reach *a* a bombardment of atom streams which, in the absence of *b*, would never strike *a* at all.

No such simple off-hand theory of pelting streams will account for any attraction. A most interesting treatise on the subject is the "*Essai sur la Synthèse des Forces Physiques*," by le P. Leray (Gauthier-Villars), which I would recommend to any of your readers who are interested in the matter.—I am, &c.,

GEORGE M. MINCHIN.

R. I. E. College, Cooper's Hill.

A NOTE ON ORTHOGRAPHY AND NOMENCLATURE.

To the Editor of the Chemical News.

SIR,—Perhaps the following memoranda, printed in the columns of your journal, may produce a useful discussion:—

Aluminum or Aluminium.—Although the former name has been much in use, the latter has been adopted by several dictionaries, on the ground that the termination *ium*, for the sake of uniformity, is preferable. But we still have the ending *um* in glucinum, tantalum, molybdenum, &c., and in all the Latin names, such as ferrum, aurum, stannum, and so on. In the present case the oxide is universally alumina, and not alumina, and aluminium seems to be objectionable on the ground that it changes an accent unnecessarily. Aluminum, moreover, to many ears, has the advantage of euphony.

Glucinum or Beryllium.—Here the first name is the original one, and should hold according to all rules of priority. The grounds of change to the latter name are not clear.

Columbium or Niobium.—The original name, given by the discoverer, was columbium. Later, Rose gave the names niobium and pelopium to two supposed new elements. Why the name which has clear priority should give way to one which perpetuates the memory of an error is by no means obvious. "Niobium" is distinctly objectionable.

Gramme or Gram.—Although a simplification of orthography is generally desirable, in this case we seem to have an exception. "Gram" is too easily misprinted and misread *grain*, and even a defect in a sheet of paper may transform the one into the other. The French spelling "gramme" is therefore preferable as conducive to precision. The phonetic form of the word is a source of dangerous error.—I am, &c.,

F. W. CLARKE.

Washington, Dec. 28, 1889.

Wire-Gauze Air-Bath.—F. Muck (*Chemiker Zeitung*).—An arrangement for applying a gentle heat to small quantities of liquid in large vessels, as on re-dissolving small precipitates in the vessels in which they were thrown down. It admits also of the application of a stronger heat. It consists of a rectangular frame of iron resting on four feet, about 22 c.m. in height. A movable sheet-iron box (about 60 by 20 c.m.) with a bottom of wire gauze, about as fine as that used in safety-lamps, four wire-gauze covers working on hinges, and four Bunsen burners. If a gentle heat is required the flames are reduced and the vessel is set upon the highest of the four covers.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 27, December 30, 1889.

This number contains merely the report of the Annual Public Session of the Academy, with announcements of the prizes awarded and of those offered.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 5.

Wine Statistics of Germany.—The continuation of a lengthy treatise, which would not present such an interest to our readers as to warrant its insertion.

Application of the Double Pyrophosphates for the Electrolytic Separation and Determination of Metals.—Dr. Albano Brand.—(See p. 2).

Lime in Tan-wares.—M. Petrowitsch.—In the examination of tanwares the only question is generally the determination of tannin. Impurities are scarcely ever sought for, as they are not intentionally added. A tanner in Zambor recently procured a large cargo of valonias from a drysalter in Vienna. A part of the lot was ground and used for tanning sole-leather. When ready the leather was found to be closely spotted over with large bluish white stains, such as have been known to be formed if the tanware is contaminated with lime. A portion of the ground valonias was sent to the author for examination. As mineral impurities might be chiefly expected in the finest portion, the sample was passed through a sieve having meshes of 1 m.m., and the fine matter was taken for examination. In 100 grms. of the ground valonias the total ash was 6.36 grms. and the lime 0.466 grm. In pure valonias the total ash was 2.554 and the lime 0.240 grm. The ash in samples of sumach ranges from 5.74 to 37.24 per cent.

A New Washing- and Absorption-Bottle.—F. A. Kühnlenz.—This paper cannot be reproduced without the accompanying illustration.

Capillary Analysis.—F. Goppelsröder.—The author's original pamphlet has been already noticed.

A New Method of Chemical Analysis with the Aid of Capillarity.—Ch. W. Phillips.—From the *CHEMICAL NEWS*.

A Systematic Course of Qualitative Analysis.—Edgar Everhart.—From the *Journal of Analytical Chemistry*.

System of Qualitative Analysis.—G. Vortmann.—No particulars are given.

Method of Calorimetric Determination by Means of Combustion in Oxygen under a High Pressure.—F. Stohmann, Cl. Kleber, and H. Langbein (*Journal für Praktische Chemie*).—No details are given.

Sources of Error in the Use of Hydrometers.—A. Fock.—The author proposes to apply a correction for the elevating power of the air. The error thus occasioned is very small, and in the most unfavourable case does not exceed a unit of the fifth decimal. The error occasioned by surface tension is more important. A formula is proposed for its correction, which, however, is in many cases inapplicable. The error occasioned by its neglect is about four units of the third decimal. The errors caused by the temperature of the air is at most five units of the fourth decimal.

A New Absorption-Apparatus in Ultimate Analysis.—J. Tsawoo White.—From the *CHEMICAL NEWS*.

A Valve Washing-Bottle.—E. Stroschein (*Chemiker Zeitung*).—No particulars are given.

A Sifting-Machine for the Laboratory.—A. Stutzer (*Zeitschrift für Angewandte Chemie*).—The arrangement requires an illustration.

The Presence of Arsenic in Glass and in Alkalies.—J. Marshall and C. Pott.—From the *American Chemical Journal*.

The Decolouration of Litmus in Closed Vessels.—R. Dubois.—The decolouration is produced by a micro-organism which, in the absence of air, has a decolourising action. In sterilised vessels litmus retains its colour.

Determination of Water in Silicates, such as Tourmaline, Vesuvian, Mica, &c.—P. Jannasch (*Ber. der Deutsch. Chem. Gesell.*).—This paper will be inserted in full.

Reduction of Ferric Salts by Means of Zinc-Powder.—Douglas J. Carnegie.—From the *Journal of the Chemical Society*.

Volumetric Determination of Phosphoric Acid by Means of Molybdic Acid.—A. Grete.—(See vol. lx., p. 310).

Quantitative Determination of Hydrosulphocyanic Acid.—P. Klasen.—Hydrosulphocyanic acid can be determined like hydrochloric acid with a solution of silver, using neutral potassium chromate as an indicator. In an acid solution (sulphuric) he adds an excess of silver solution, then iron-alum, and titrates back with centinormal solution of ammonium sulphocyanide until the colour appears. Both the above methods are of little practical value, since hydrochloric acid must not be present. A method for the determination of hydrosulphocyanogen can also be founded upon its ready oxidation in an acid solution by means of potassium permanganate, forming hydrocyanic acid and sulphuric acid. The result obtained is too low if the concentration is less than decinormal.

New Method for Determining Nitrites.—T. Cuthbert Day.—From the *Journal of the Chemical Society*.

Determination of Nitric Acid.—H. N. Morse and A. F. Linn.—From the *American Chemical Journal*.

Quantitative Determination of Chloric Acid in Chlorates by Means of a Copper-Zinc Element.—C. H. Bothamley and G. R. Thompson.—From the *Journal of the Chemical Society*.

Preparation and Properties of Fumaric.—R. Reichwald.—Fumaric is readily soluble in chloroform, less readily in benzene, but it is sparingly soluble in water, alcohol, ether, and petroleum ether. With strong sulphuric acid it gives a splendid violet colour. If covered with Froehde's reagent it turns violet and then dark green; with vanadic sulphuric acid it becomes a persistent emerald green, turning, after some hours, to a more yellowish shade. By strong sulphuric acid it is turned at first pale yellow and then light brown.

The Ultimate Analysis of Organic Bodies by Means of Electricity.—M. Levoir.—The weighed substance is placed in a platinum tube placed vertically among three spirals of platinum in a vertical glass tube. The wire is $\frac{1}{2}$ m.m. thick and 1 m. long, and is raised to redness by a dynamo. The combustion is effected by means of a current of oxygen. The products of combustion are received in absorption-tubes in the ordinary manner.

Conduction of Elementary Analyses by the Combustion of Organic Substances with Oxygen under High Pressure.—Arnold Eiloart.—From the *CHEMICAL NEWS*.

The Kjeldahl Determination of Nitrogen.—M. L'Hôte, C. Vidette, E. Aubin, and L. Alla.—From the *Comptes Rendus*. The matter has been already inserted.

Determination of Sugar by Fermentation.—M. Jodlbauer (*Dingler's Journal*).—The author has studied

the conditions under which a definite relation is obtained between the quantity of sugar fermented and the weight of the carbonic acid formed. He concludes that under certain conditions the products of alcoholic fermentation are constant. These conditions are the use of a powerfully developed yeast, which has undergone no loss of its tissues or of the protoplasmic contents of its cells by autofermentation. The preservation of a certain proportion between yeast and sugar; the yeast must not exceed 50 per cent of the sugar. Free oxygen must be excluded and a suitable nutritive substance must be supplied. The best temperature is 34° and the most favourable concentration is 8 per cent. Of the products of fermentation carbonic acid admits of the easiest and most exact determination. Saccharose and anhydrous maltose yield 49.04 of carbonic acid, and dextrose 46.54 per cent. Saccharose requires twice as long a time for fermentation as maltose and dextrose.

Determination of Alkalies in Waters.—Fr. Muck.—For this purpose an indirect method is mostly used which depends on converting the residue of the evaporation of several hundred c.c. into sulphates. From the weight thus obtained is deducted the weight (determined in another portion of the water) of the silica and the potassium and magnesium sulphates present. If no appreciable quantities of alumina and iron are present the remainder is the weight of the alkalies determined as sulphates. In the conversion of the residue into sulphates it is difficult to hit the exact quantity of sulphuric acid to be used. The author overcomes this difficulty as follows:—He moistens the residue with alcohol containing sulphuric acid (3 drops to 1 c.c.) and burns off the alcohol. If the quantity added is insufficient the resulting saline mass is dry; if sufficient it is moist, and vapours of sulphuric acid are given off before the alcohol is entirely consumed. Until this takes place the moistening and burning off are repeated, using, each time smaller and smaller quantities of the sulphuric alcohol. The final ignition and treatment with ammonium carbonate takes place in the ordinary manner.

Detection of Foreign Colouring-Matters in Wine.—A long compilation from the *Comptes Rendus*, the *Journal de Pharmacie*, the *Bulletin de la Soc. Chimique*, and the *Chemiker Zeitung*.

Determination of Free Hydrochloric Acid in the Human Gastric Juices.—Boas mixes 5 to 6 drops of the secretion with two or three drops of a solution of 10 grms. resorcin, 3 grms. sugar, and 3 c.c. alcohol in 100 c.c. water, and evaporates to dryness in a small platinum capsule over a small flame. If hydrochloric acid or some other powerful mineral acid is present there is produced a fine rose or scarlet surface, which gradually loses its colour on cooling. This reaction indicates 1-200th per cent of hydrochloric acid. Organic acids do not produce it. For the quantitative determination Sjögqvist takes 10 c.c. of the filtered fluids of the stomach, mixes them in a silver or platinum capsule with a slight excess of barium carbonate, and evaporates them to dryness on the water-bath, thus converting the free acids into barium salts. By carbonising the residue and igniting for a few minutes the organic barium salts are converted into carbonates. The cold carbon, comminuted as much as possible with a glass rod, is extracted at a boil with 10 c.c. of water, poured on a filter, and washed until the filtrate makes up 50 c.c. In this solution the barium is determined, and shows the proportion of hydrochloric acid originally present. The author has also developed a volumetric method for the same purpose.

Sensitiveness of the Reactions for the Sugar in Urine.—G. Rosenfeld.—The author gives the preference to Böttcher's bismuth test.

Re-determination of the Atomic Weight of Zinc.—H. N. Morse and W. M. Burton.—From the *American Chemical Journal*. The value decided on is 65.3.

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. vii., No. 3.

This issue contains no chemical matter which we do not find elsewhere.

MISCELLANEOUS.

Ozone.—According to a letter in the *Electrical Review*, Ernst Fahrig has discovered a method of producing ozone on the large scale, and at a cost which will admit of its general industrial application. He hopes also to condense it, so as to render it portable. We regret to find that the inventor insists on applying to ozone the long and vague name "electrical gas." Chemists cannot sanction the application of a new name to any substance merely because it has been produced in a novel manner.

Lectures on Coal-Tar Products.—The First of a Course of Twelve Lectures on Coal-Tar Products was delivered by Professor R. Meldola, F.R.S., F.I.C., F.C.S., at the City Guilds Technical College, Finsbury, on Thursday evening, January 16th, 1890, to be continued on successive Thursdays. The Lectures will commence at 7.30 p.m. The raw materials used in the manufacture of artificial colouring-matters and other commercial products will be dealt with and their technology described. The lectures will be adapted for those engaged in the industry, as well as for manufacturers of fine chemicals, and for students of technical chemistry.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Medical, 8.30.
— Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.
TUESDAY, 21st.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Society of Arts, 8. "Tea, Coffee, and Cocoa Industries of Ceylon," by John Loudoun Shand.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
WEDNESDAY, 22nd.—Society of Arts, 8. "Vision-testing for Practical Purposes," by R. Brudenell Carter, F.R.C.S.
— Geological, 8.
THURSDAY, 23rd.—Royal, 4.30.
— Royal Society Club, 6.30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Sculpture in Relation to the Age," by Edwin Roscoe Mullins.
FRIDAY, 24th.—Quekett Club, 8.
— Royal Institution, 9. "The Scientific Work of Joule," by Prof. Dewar, M.A., F.R.S.
SATURDAY, 25th.—Royal Institution, 3. "The Natural History of the Horse, and of its Extinct and Existing Allies," by Prof. Flower, F.R.S., &c.

FOR SALE.—THE CHEMICAL GAZETTE.
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THE CHEMICAL NEWS.

VOL. LXI. No. 1574.

SPECTRO-ANALYTICAL DEMONSTRATION OF TRACES OF A NEW ELEMENT

BELONGING TO THE

ELEVENTH SERIES OF MENDELEEF'S TABLE,
AND OCCURRING ESPECIALLY IN TELLURIUM AND
ANTIMONY, BUT ALSO IN COPPER.

By Dr. ANTON GRÜNWALD.

THE author concludes that the assumed elements tellurium, antimony, and copper contain traces of a new, hitherto unknown element, X, of Mendeleef's eleventh series. It is on the one hand related to tellurium, and on the other hand very closely to bismuth. It is very probably identical with the element of group VI., series 11, having the approximate atomic weight 212, and also with Dr. B. Brauner's "Austriacum" recently discovered in tellurium. The author gives the wave-lengths of 16 rays of the new substance observed in the ultra violet between 2768·9 and 2159·7.—Reprint from the *Proceedings of the Imperial Academy of Sciences in Vienna*, Vol. xcvi., Part II., October, 1889.

THE APPLICATION OF DOUBLE PYROPHOSPHATES FOR THE ELECTROLYTIC SEPARATION AND DETERMINATION OF METALS.

By Dr. ALBANO BRAND.

(Continued from p. 29).

II. Separation of Manganese from other Metals.—The property of manganese of being electrolytically deposited as peroxide from a strongly ammoniacal solution of the double pyrophosphate, but of remaining in solution as a double salt in presence of free acid, points to a twofold way for the separation of manganese from other metals; in the case of those whose double salts bear the addition of ammonia, the manganese is first deposited as peroxide, whilst the metal is first precipitated in those which can be reduced from an acid solution.

1. Manganese from Nickel, Copper, Cadmium, Zinc, and Mercury.—If the ammoniacal solution of the double ferrous and ferric salt is submitted to electrolysis, there ensues, besides the reduction of the metal at the cathode, a separation of a brownish red basic iron salt at the anode. This abnormal decomposition does not entirely cease in presence of manganese and with the feeble currents required for the separation of manganese peroxide, and renders the separation of manganese and iron in this manner impossible.

The double cobalt salt behaves in an ammoniacal solution in presence of manganese just like the double iron salt, although on the electrolysis of the cobalt salt alone the metal only is deposited.

The separation of nickel from manganese in a solution of the double salt with 15 per cent of strong ammonia proceeds very evenly. Even with very feeble currents a little nickel is deposited on the cathode. After pouring off the liquid into another capsule, the reduction of the nickel is completed with more powerful currents. On the suspended electrode 0·3 grm. nickel can be conveniently deposited and weighed; an electrode of strong platinum wire is particularly suitable.

Copper and manganese can be conveniently determined in the same solution. In order to separate out the copper in a compact condition, the strength of the current must be very low at the beginning, and the capsule must be taken as cathode. For large quantities of copper or manganese the method of separation given under II., 2.

The separation of cadmium, zinc, and mercury, or of several metals conjointly from manganese, is effected in the same manner as given for nickel.

2. Manganese from Copper, Cadmium, and Mercury.—The property of manganese of remaining in solution as manganic pyrophosphate (or double manganic salt) on the electrolysis of an acid solution which at the same time contains pyrophosphoric acid, enables it to be separated from all metals which can be determined by the electrolysis of an acid solution.

The separation of manganese from iron, nickel, and cobalt in a solution containing little free pyrophosphoric acid is possible, according to the author's experiments, but requires currents of disproportionate strengths for the separation of the three metals.

The separation of manganese from copper and cadmium succeeds readily in a sulphuric solution, and that from copper and mercury in a nitric liquid. The solution of the pyrophosphates is acidified with the corresponding acid, and copper is reduced with a current of 3—4 c.c. detonating gas per minute, mercury with 0·2—0·5 c.c., and cadmium as laid down in I., 6.

After evaporating off the larger quantity of liquid which has been obtained on washing without an interruption of the current, the manganic oxide is reduced in heat by oxalic acid, and the manganese is separated as peroxide by a feeble current from the solution mixed when cold with ammonia. The conversion of a little pyrophosphoric acid into orthophosphoric acid in presence of nitric acid does not interfere with the determination.

3. Manganese from Iron and Cobalt.—The abnormal decomposition of the double iron and cobalt salt renders the separation of both from manganese impracticable in an ammoniacal solution.

In experiments for the prevention of the separation of a basic iron salt at the anode by the addition of various salts it was observed that if the solution of the pyrophosphates in an excess of the precipitant contains ammonium oxalate, the manganese remains in solution as a double salt, as it takes place in presence of free acid.

This observation agrees with that of Prof. A. Classen, as stated in one of his earlier publications on the application of the double oxalates in electrolysis. He writes:—"The separation of iron and manganese by the electrolysis of the double oxalates is practicable only when the formation of manganese peroxide is prevented until the greater part of the iron has been thrown down. This can be effected by the addition of sodium phosphate, or most readily by means of a large excess of ammonium oxalate."

In the electrolysis of the solution containing ammonium oxalate there is first formed, on the decomposition of this salt, ammonium carbonate; but so readily as it occasions precipitations in the solutions of the double manganese pyrophosphate, such do not occur on the simultaneous presence of both the above salts except the bulk of the oxalate has been decomposed and much manganese is present.

For the separation the solution containing manganese and iron is mixed with such an excess of sodium pyrophosphate that the precipitate formed at first is completely dissolved. If the solution of the metals contained free acid, it should be neutralised as completely as possible before the addition of the sodium pyrophosphate, as a subsequent addition of ammonia or of ammonium carbonate is excluded. The solution is mixed either at once or partly during the electrolysis with 4—8 grms. ammonium oxalate.

In order to avoid washing without interruption of the current the metal is best deposited upon a suspended

electrode of round platinum wire (not foil), and, after the completion of the reaction, it is quickly plunged into distilled water. The author easily succeeded in determining 0.2 grm. of iron by means of an annular electrode of wire 1.5 m.m. in thickness, weighing 14.5 grms., and having a surface of 7.8 square c.m. A spiral of four turns of wire 2 m.m. in thickness, with a surface of 24 square c.m., and weighing 27 grms., would suffice for more than $\frac{1}{4}$ grm.

When much iron is present we begin with a current of 5 c.c. detonating gas per minute: towards the end a current of 15—20 c.c. is requisite.

After removal of the iron the solution in the capsule is faintly acidified with sulphuric acid, and the red double manganic salt is reduced by oxalic acid (with the aid of heat) to a manganous salt (I., 4). After adding 15 per cent of strong ammonia the manganese could be at once determined in the same capsule as manganous-manganic oxide.

Attempts to ascertain the proportion of manganese by titration (addition to the red solution of potassium iodide and hydrochloric acid and determination of the iodine liberated) did not succeed, but they rendered it very probable that the red double salt contains the manganese in the manganic stage, as the proportion of oxygen is regularly found a little lower than corresponds to this stage.

In a solution which contains the double ammonium salt of manganese there is formed, without any addition on electrolysis, a double oxide salt which undergoes no further decomposition. This solution is not suitable for the separation of manganese and iron, as, in presence of iron, after its deposition, a white manganic salt is found firmly deposited.

The separation of iron requires much attention, and some practice is needed to obtain regularly good results. But the method admits of use if the conditions above laid down are carefully observed, and this the more readily the less iron is present.

4. *Cadmium from Zinc, Iron, Nickel, and Cobalt.*—The readiness with which cadmium can be separated electrolytically from a sulphuric solution facilitates its separation from all metals which are not reduced in a sulphuric solution.

By means of the double pyrophosphatic salts, zinc, iron, nickel, and cobalt may be distinctly separated from the liquid after removal of the cadmium, the solution of the double salts having been first supersaturated with ammonium carbonate. It is indifferent whether the sodium pyrophosphate is added before or after the separation of the cadmium.

5. *Cadmium from Zinc, Nickel, and Manganese.*—The process is the same as the separation from zinc or nickel alone, but in this case sodium pyrophosphate is added before the separation of the cadmium to keep the manganese in solution. The liquid obtained on washing (without interrupting the current) is mixed with oxalic acid and heated for the reduction of the manganic salt; then, when cold, supersaturated with ammonia and treated as in I., 4.

6. *Iron, Nickel, Cobalt, and Zinc from Aluminium, Magnesium, and Uranium.*—Among the metals of the alkaline earths only magnesium forms a pyrophosphate readily soluble in an excess of the precipitant, which bears an addition of ammonium carbonate but is precipitated by ammonia. The uranium double salt behaves similarly. Aluminium pyrophosphate is also soluble in ammonia.

If a solution mixed with ammonium carbonate and containing, along with the double pyrophosphates of iron, nickel, cobalt, or zinc, the corresponding salts of aluminium, magnesium, and uranium is submitted to electrolysis, the former are reduced whilst the latter remain in solution. A separation is thus readily effected, but the presence of the pyrophosphoric acid occasions difficulties in the subsequent determination of the metals which remain in solution.—*Zeitschrift für Analytische Chemie.*

A SENSITIVE TEST FOR CERTAIN IMPURITIES IN MERCURY.

By Dr. G. GORE, F.R.S.

VARIOUS investigators, including Wheatstone, Jules Regnault, Gauguin, Crova, Robb, Lindeck, and Hockin and Taylor (*Journal Telegraph Engineers*, 1879), have examined the electro-motive forces of metallic amalgams in acid and saline liquids, and the latter investigators have shown that 1 part by weight of zinc in 23.6 million parts of mercury is electro-positive to pure mercury in a solution of zinc sulphate.

My object in the present research was different from those of previous investigators, and was briefly to ascertain and illustrate the degree of delicacy of the voltaic energy method when employed as a means of detecting the presence of certain metals in mercury.

Two portions of very pure mercury in an electrolyte were connected by insulated platinum wires with an ordinary astatic torsion galvanometer of 100 ohms resistance, and a sufficiently minute proportion of a very dilute amalgam, of known strength, of one of the particular metals with some of the same mercury was added to one of the portions of mercury, to cause the needles of the instrument to be just visibly deflected whilst being viewed with the aid of a magnifying glass. The volume of water employed in each electrolyte was 120 c.c. The following Table shows the results:—

One part of—	1.0 grain of HCl or H ₂ SO ₄ in 120 c.c. of water. Parts of mercury.	10 grains of KCl in 120 c.c. of water. Parts of mercury.
Mg	110,274,000,000	13,430,858,806
Zn	104,950,000,000	18,034,482,758
Cd	184,828,432	10,404,225
Sn	38,900,000	8,831,632
Cu	15,484,375	1,640,160
Bi	9,762,300	1,621,000
Pb	5,651,149	1,050,341
Ag	905	79

The minimum degree of electro-motive force required to visibly move the needles was found by heating one end of a single thermo-electric couple of iron and pure copper 9.6 centigrade degrees higher than the other end, or of one of platinum and copper 49.5° C. higher than the other, the opposite ends of the couples being immersed in vessels of oil, and was in each case equal to about 0.00013258 volt. This, therefore, was approximately the degree of electro-motive force of amalgam of 1 part of zinc dissolved in about 105,000 million parts of mercury, or of 1 part of magnesium with about 110,000 million parts of mercury, when opposed to pure mercury in solutions at atmospheric temperature of sulphuric or hydrochloric acid of the degrees of strength given. With the aid of a much more sensitive galvanometer, the influence of very much smaller proportions of impurity upon the amounts of voltaic energy and electro-motive force might be detected.

In the above Table the order of voltaic energy of the metals is substantially the same as that of the metals alone and unamalgamated. With each amalgam the amount of energy gradually declined, but recovered on stirring the mixture; the decline was quickest with the most dilute ones. An amalgam of magnesium with 1605 times its weight of mercury rapidly became covered with a thin film of black suboxide of magnesium on exposure to the air.

As the influence of the above minute proportions of all the metals, except silver, may be thus readily detected, I have employed this method to test the purity of mercury. I took about 2000 grains of mercury, containing, dissolved in it, 6 grains of a mixture of the above eight metals, distilled off the mercury, and then used the product in place of the amalgam in the potassium chloride solution

in the above manner; the galvanometer needles were very slightly affected, but after a second distillation of the mercury the needles were not visibly moved.

THE CHEMICAL PROBLEMS OF TO-DAY.*

By VICTOR MEYER.

(Concluded from p. 31).

THE discovery of the system of the elements leads us back to the question whether the chemical elements are separate worlds in themselves or whether they represent different forms or conditions under which one ultimate substance exists; a question that has occupied the philosophical mind since very early times. The same question was raised anew by the discovery of spectral analysis. Whosoever regards the numerous lines of the spectrum of a metal will hardly be convinced that the metal from which they emanate should be an eternally indecomposable element. In a similar manner the compound nature of the elements is indicated by comparison of the regularities in numbers of the atomic weights with the homologous series of organic chemistry.

In the pursuit of this question, which, since Prout's hypothesis and the surprises offered by Stas's determinations of atomic weights, has not been allowed to rest, positive results are not to be found. The decomposition of substances called elements into simpler ones has not been accomplished.

Nevertheless, something has been achieved, since an increased interest has been drawn towards pyro-chemical research.

To-day, new methods of experiment permit of a comparatively easy determination of the vapour density, and consequently of the molecular state of the substances at the highest temperatures.

Numerous inorganic compounds, above all the very elements, have been studied in regard to their vapour density at a white heat.

While many of them, as oxygen, nitrogen, sulphur, and mercury, remain unchanged under such conditions, the molecules of chlorine, bromine, and iodine respectively, were split into two atoms, in conformity with Avogadro's surmise of the compound nature of elementary molecules.

In the same manner, the vapour density and the molecular condition of the less volatile substances, zinc, thallium, antimony, and bismuth, was successfully determined at a white heat.

Careful research resulted in the exposure of the old fallacy of the existence of a sulphur molecule containing six atoms.

But how many of the problems which crowd around us at this point are for the time being entirely beyond the reach of the experimenter!

To-day, pyro-chemical work is limited to a temperature of 1700° C., because vessels of porcelain and platinum, to the use of which we are limited, fuse above that temperature. The possibility of performing quantitative experiments at these temperatures seemed to us some years ago to be an unexpected progress, but to-day we complain that the trivial cause of a want of proper vessels forbids us to increase the temperature up to 2000° or 3000° C. There is no doubt that we should arrive at new unthought of facts, that the splitting of still other elementary molecules would be possible, that a new chemistry would be revealed to us if, being provided with vessels of infusible material, we could work at temperatures at which water could not exist, and at which detonating gas would be a non-inflammable mixture!

* An Address delivered at Heidelberg at the First General Session of the Sixty-Second Meeting of the Association of German Naturalists and Physicians, Sept. 18, 1889. Translated, by L. H. Friedburg, from the *Deutsche Rundschau*, Nov., 1889.

Let us now enter other fields of physical chemistry. Golden fruit, daily increasing, has been harvested upon this field during these latter days. Again we see Van't Hoff take the lead. His keen eye has enabled us to penetrate the nature of *solution*, which forms the beginning of a new epoch in molecular physics. The quintessence of his discoveries may be thus expressed:—

"Solutions of different substances in the same liquid, which contain in the same volume an equal number of molecules of the dissolved substance, show the same osmotic pressure, the same vapour pressure, and the same freezing-point."

This surprising generalisation offers the possibility of determining the true molecular weight of substances by experimenting upon them in *solution*, while heretofore this has only been possible by transforming them into the gaseous state, hence only for volatile substances, since dilute solutions behave in regard to the molecular state of the dissolved substance like gases.

In this manner, new methods are given for the determination of molecular weights, which we are now able to determine by means of measurements relating to the freezing-point, the vapour pressure, or the osmotic pressure of a solution of the substance to be tested.

These results are of the highest possible practical importance for chemistry, since they widen in an unexpected manner the possibility of the determination of molecular weights, and in a still higher degree we are surprised by the elucidation which they offer in regard to the nature of *solution*. Clausius had already admitted within narrower limits, that in solutions of electrolytes some of the dissolved molecules were decomposed into their ions, but now this has been proved in a larger measure, particularly by Arrhenius. What a change our conceptions will have to undergo if we have to accustom ourselves to regard a dilute solution of sodium chloride as one containing not undecomposed molecules of this salt, but separated atoms of sodium and chlorine!

We owe these revolutionising innovations to the investigations of Van't Hoff, Arrhenius, Ostwald, Planck, and de Vrie, but, in regard to experimental research, especially to the splendid work of Raoult, which during recent years has effected this mighty theoretical progress.

Thus we see Physical Chemistry moving on in weighty development. Special laboratories are opened for her, and a special journal also has been started, which is open alike to the records of experiment and to theoretical discussion. Through the foundation of this organ, physical chemistry has been furthered in a most active manner. All the questions of the time, and all those in dispute belonging to this department of science, receive in this paper a thorough discussion. Dynamical-chemical questions are successfully studied, a significant impetus is given to the study of structure and affinity (widened as our knowledge of the nature of solutions has made necessary), by means of the study of the relations between chemical nature and electric conduction.

The inquiry into the intimate relations that exist between physical and chemical properties, which was inaugurated half a century ago by Hermann Kopp, is now being deepened and widened.

It is true that the great hopes which sprang from the study of thermo-chemical questions have so far been only partly fulfilled, but consecutive measurements offer more clearness also in this case.

There is no field of our science in which we may expect greater revolutions in the time near at hand than in that of physical chemistry! The value of these for general chemistry will be greater in proportion as the representatives of the same will recognise their task in this: above all to remain upon the chemical standpoint, and to improve chemistry by the application of physical modes of thought and experiment. Those who tried to further the progress of chemistry by the use of physical methods, but with insufficient considerations for chemical relations, have been led into serious errors. The respect

due to work of the highest merit, continued for years, has thus been lessened. Apparently, this has even been overdone, and it is much to be deplored if the interest of chemists for physical chemistry should be diminished because some of its representatives are inclined to overrate the value of their results. He who swims in the midst of high waves is unable at times to see over the crests.

Innumerable, also, are the problems which meet us in the domain of organic chemistry.

After the astonishing harvest of synthetical results which has been reaped here, hardly any problem of synthesis seems unapproachable. Since the artificial preparation of alizarin by Graebe and Liebermann, of indigo by von Baeyer, of conine by Ladenburg, of uric acid by Horbaczewski, and particularly by Behrend, since Emil Fischer and Kiliani have elucidated the chemistry of the sugar group, and Wallach that of the terpenes, we may well look hopefully for a clearer knowledge of the bodies comprised under the name albumen, and to its synthesis.

But even such success tends only to render us more modest, since they show us at the same time how narrow are the limits within which chemical synthesis moves. Assuming even that the preparation of albumen had been achieved—how infinitely far we should still be from a conception of the nature of *organised* bodies! Perhaps science is separated by an impassable chasm from the artificial preparation of a simple cell. Such an achievement lies at least beyond the sphere of chemistry.

But shall we really never succeed in sounding the process of *assimilation*, which in spite of its simplicity presents itself to us so enigmatically? Will it be found impossible to prepare artificially in our laboratories from carbon dioxide and water, sugar and starch, a process which nature performs unceasingly in the green parts of plants?

The chemist, however, should not step prematurely upon the field of biology, while so many great problems remain untouched in his own peculiar sphere of investigation.

The *method* of research in organic chemistry, in spite of the brilliant successes already recorded, forces us even to-day to confess that only a very minute proportion of known substances is within its reach. In order to isolate an organic substance we are generally confined to the purely accidental properties of *crystallisation* or *volatilisation*. Have not those thousands of amorphous substances, which cannot be characterised by any chemical property, and which the chemist is forced to lay aside because he is unable either to purify them or to transform them into volatile or crystallisable bodies; have they not the same claim upon our interest as their more beautiful and more manageable comrades?

The most significant progress of organic chemistry does not consist in single discoveries, nor in further expansion of synthetical success. What we want are:—*New methods for recognising the individuality of substances.* The black substances of earthy nature, the innumerable formless and resinous products in the bodies of plants and animals, the colouring matter which gives beauty to flowers, all of these to-day mock our efforts to know them; they will form a new and inexhaustible field for the prosecution of chemical research, when *methods* shall have been found with which to begin this research.

And, as in organic chemistry, so in *mineral chemistry*, every step leads to questions, which we have, as yet, no means of answering. The synthesis of minerals and of rocks has made important progress, it is true, and this, as well as the application of the doctrine of structure to the study of mineral species, gradually leads to the understanding of their constitution. But we are, as yet, unable to use, in the study of minerals, the method of *analytical decomposition* which has been so successfully used to study the constitution of organic substances, and, above all, we lack the least knowledge in regard to the *true molecular weight* of minerals.

Quite recently we have been presented with no less than three new and fruitful methods for the determination of the molecular weight, but not *one* of them gives us an indication of the true molecular weight of the most simple oxides, such as silicic anhydride or calcium oxide.

We know to-day very well that silicic anhydride cannot have the formula SiO_2 , that this must be multiplied by a very large factor; but of the numerical value of this latter we have no indication. And thus also in mineral chemistry we must aim, not exclusively at finding new *facts*, but *new methods of research* in the first place, if a period of new discoveries is to be attained in this branch of our science.

But how can we conclude this brief review without mentioning also the *applications of chemistry to the industrial arts*, the progress of which have mainly contributed to spread the splendor of our science most widely? The infinite variety of the tar colours, surpassing the colours of flowers in number and brightness, is daily increased by new discoveries. The industry of these forms the most brilliant triumph of purely scientific laboratory work applied to manufactures. This industry, in the simplest manner, and on the largest scale, performs the synthesis of compounds the complex nature of which is indicated by the names they bear. The unscientific man is frightened when a beautiful and brilliant dye is referred to as *Hexamethylmethoxytriimidotriphenylcarbinol*; for the initiated there lies in this unpleasant name a full account of the synthesis and the constitution of the dye.

Industry has learned to derive not only colours but healing medicines also from coal-tar. Antipyrin, discovered by Knorr, upon the basis of Emil Fischer's fundamental research upon the hydrazins, brings to thousands suffering from fever, relief at least, if not cure. Let us hope that the time is not far distant when *real* fever curatives, which, like the natural alkaloids of the cinchona bark, not only temporarily *suppress* the disease but really *cure* it, may be prepared by synthesis. Until then be patient and do not chide chemistry if, for the time being, she offers only silver instead of gold.

Events in this field of the great chemical industries are significant. We are the witnesses of a great combat taking place between the older process of Leblanc for the preparation of soda and the new one of Solvay, called the Ammonia-Soda process. The intelligence and inventive genius of manufacturers have added, under the pressure of this competition, a large number of improvements to the manufacture of sulphuric acid and of soda, and new and valuable methods for the preparation of chlorine. Here, more than in any other branch of chemical industry, the struggle for existence is fierce.

The manufacture of iron, that most important chemical industry, is transformed by innovations. The imposing changes wrought by the older process of Bessemer, by the new one of Thomas, are they not based purely upon chemical reactions? The grandest application of a complicated chemical reaction to a great manufacture is, perhaps, the dephosphorising of pig-iron by lining the Bessemer converter with basic material, an invention which we owe to Thomas and Gilchrist. From this, again, agriculture derives an advantage in the use of the Thomas slag containing the phosphorus which heretofore rendered iron-ore less valuable. This, then, is truly a transformation of stone into bread, similar to the older manufacture of soluble fertilisers from mineral phosphates. Nevertheless, the era of bliss which was prophesied three years ago at the Berlin meeting of naturalists by our illustrious colleague, Ferdinand Cohn, has not yet dawned. He held that all struggles for existence amongst men, arising from want of food, the bread question, will be done away with when chemistry shall have learned to prepare starch from carbon dioxide and water. But since time immemorial the farmer has been occupied in this very chemical industry, and it would hardly be great progress if the farm were merely replaced by a

chemical factory. But we may reasonably hope that chemistry will teach us to make the fibre of wood a source of human food.

Indeed, if we consider how small is the quantity of starch which the grain furnishes us, and further that the wood fibre has exactly the same chemical composition as starch, we see the possibility of increasing the production of food infinitely by solving this problem: to transform cellulose into starch.

If this problem were solved we should find an inexhaustible source of human food in the wood of our forests, in grass, and even in straw and chaff. The beautiful researches of Hellreigel have recently disclosed the fact, which in former times was disputed, that certain plants transform atmospheric nitrogen into albumen and that this process can be improved by suitable treatment.

The increase of albumen in plants, according to a plan, together with the production of starch out of cellulose—this would in reality signify the abolition of the bread question.

May it some day be granted to chemistry, through such a discovery, to inaugurate a golden age for humanity.

I have tried to give a review of the most important problems which are set before chemical science. I have mentioned a goodly number, but the short time of one hour permits me to touch but slightly upon the greater ones. There are so many problems before us which await an immediate solution as to justify what I said in the beginning, that to-day the chemist has no time so complain because the epoch of a mathematical treatment of his science has not yet arrived.

Nevertheless, the brilliant successes which have been gained, the wonderful results which are immediately within our reach, have not the power to turn our eyes from this final problem.

The Newton prophesied to chemistry by Emil du Bois Reymond, may he appear at a later period; until he comes, may many a generation honourably plough on in the sweat of its brow! We must remember that nature is not understood by us until we are able to reduce its phenomena to simple movements, mathematically traceable.

The time will come, even for chemistry, when this highest kind of treatment will prevail. The epoch in which the foremost impulse of its research was a serenely creative phantasy will then have passed; the joys, but also the pangs and struggles, peculiar to youth, will have been overcome.

Re-united to Physics, her sister science, from whom her ways at present are separated, Chemistry will run her course with firm and unflinching steps.—*Journal of American Chemical Society*, vol. xi., No. 7.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, January 4th, 1890.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of

samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 168 samples examined were found to be clear, bright, and well filtered.

The condition of the water supply to the Metropolis during the past month has been wholly satisfactory. What little difference of character has been observable between the supply of the past month and that of the two preceding months, is in the direction of a greater degree of freedom from colour-tint and from excess of organic matter, as determined alike by estimation of the quantity of oxygen absorbed and of organic carbon present. As regards the Thames-derived supply more particularly, though falling off slightly in November and more than retrieving itself in December, it has not presented any difference of composition that can be regarded as at all noteworthy during the past three months. Just now, indeed, it is for the period of the year of exceptionally high quality, the maximum proportion of organic carbon present in any one sample examined being only 0.155 part, and the mean proportion 0.143 part, in 100,000 parts of the water.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

THE ESTIMATION OF MINUTE QUANTITIES OF GOLD.*

By Dr. GEORGE TATE, F.I.C., F.C.S.,
Principal at the College of Chemistry, Liverpool.

At a recent criminal trial, wherein experts referred frequently to thousandths of a grain, Mr. Justice Stephens ventured the opinion that the mind untrained in the observation of minute quantities could not comprehend so minute a fraction of what many conceive as being the least ponderable quantity.

As a person that is accustomed to weigh or handle fractions of an ounce, or possibly only of a pound, cannot place before you the most approximate estimate of a grain, so in like manner a chemist, accustomed to weigh only to the hundredth of a grain, would generally fail to form an approximate estimate of a thousandth of a grain. I say this since, although the wonderfully fine workmanship of a good assay balance permits of the estimation of a thousandth of a grain, still such minute portions of chemical substances are commonly estimated by the observation of an eye trained to observe colour, opacity, or other comparative physical effects brought about by the action of reagents, chosen according to the nature of the substance brought under analytical tests. It is virtually only by comparison, by having some bulk, colour, or appearance as a standard of quantity, that the eye can estimate weights either large or small. I purpose endeavouring to show you how minute a quantity of certain substances is capable of recognition; and to show how, by suitable means, such minute quantities as the one ten-thousandth, or even the one hundredth-thousandth

* A Paper read before the Liverpool Polytechnic Society, November 1889.

of a grain, may be estimated with such accuracy and certainty as I think will satisfy the most captious mind.

For the recognition of these minute quantities, what are termed colour reactions are certainly the most sensitive, and therefore most extensively employed by chemists.

I have formed an estimate of the sensitiveness of certain of these reactions, so that their capabilities might be demonstrated to you. I have here portions of brucine, strychnine, iron, and copper in the form of salts, obtained by sub-division of dilute solutions of known strength; these portions contain therefore known quantities of matter. Each of these quantities give with specific reagents distinct colour reactions, indicating, with more or less conclusiveness, the presence of the respective substances.

These powers of such colour reactions, for the recognition of minute quantities of certain chemical bodies when isolated in a fair state of purity, are unsurpassed, saving by the powers of the microscope and spectroscope. When applied, however, to quantities extracted from an ounce or more of organic or inorganic matter, these colour methods would fail to form more than the most approximate estimate of the ten-thousandth of a grain, and could enable me to only state (not in every case with scientific precision) that some minute trace of the substance was present in the ounce weight of matter.

The microscope, however, now an instrument with which a scientific or analytical chemist cannot dispense, can, in many cases, recognise and identify with conclusiveness far less than the millionth of a grain of chemical matter, and estimate its weight with a fair degree of accuracy. I have, during the past year, had frequent occasion to estimate minute quantities of gold, imponderable upon the best assay balances, and have lately proved, to my satisfaction, the general accuracy of my method of working. I purpose demonstrating to you this method of estimating gold, and to lay before you facts and figures that I trust will convince you of the accuracy of my work. It may appear to some a "fancy" method of no practical utility, but when we consider the needs of the gold prospector, and how any method for enhancing the accuracy of estimation lessens the labour involved in an assay or chemical test, any such process is at least worthy of trial.

The method I have elaborated is virtually the system of measurement of gold, after fusion and when in an approximately spherical form, described in Plattner's work on the blowpipe and in other works on assaying. As there described, the weight of a bead of gold is estimated from its diameter, obtained by placing the bead above a divided scale of two divergent lines. The method is no doubt familiar to all assayers, and I think all that have tried it will agree with me that with small beads of gold two independent observations may differ often by 1000 per cent. I have found that by employing a compound microscope to largely increase the apparent size of the prills or beads, and an eyepiece micrometer as a scale, that the measurement method becomes one possessed of scientific accuracy and of powers far beyond that of the very finest balance ever constructed. To convince you of this, I have here beads of gold, each respectively the 1-100th, 1-1000th, 1-10,000th, 1-100,000th, and 1-1,000,000th of a grain, which I may guarantee to be accurate to those weights within 10 per cent, even in the case of the smallest weight.

The magnitude of the smallest of these weights may be better conceived when I state that it is quite invisible to the unaided eye, and that one thousand of them would be required to distinctly turn a delicate assay balance, and that the error in estimating the weight of these thousand beads could, only by the most elaborate system of weighing, be made to fall within 20 per cent.

These beads or prills are, what I may term, standard weights, and have been accurately measured with the

microscope; so that by comparison with these, the weights of gold prills such as may be obtained as the result of an assay, may be accurately estimated.

Preparing the Standards.—To obtain these standard beads I take a weight of pure gold (e.g., 0.1 grm. or 1 grain) that can be accurately weighed within 1 per cent on an ordinary analytical balance, or within an error of 0.1 per cent on an assay balance, and alloy it with about 100 times its own weight of pure lead, either by fusion upon a scorifier or in a small crucible. After weighing the alloy obtained I calculate what weight of it contains the quantity of gold I require for the standard bead or prill (e.g., 0.1 m.grm. or 0.001 grain, according to the system of weights adopted).

For the lead, ordinary assay lead or the lead obtained from litharge by reduction, may be employed for gold-lead alloys of one per cent, without introducing an error of more than one per cent in the weight of the bead obtained from them.

This slight error arises from the presence of a trace of silver in so-called pure lead or in litharge lead; this error becomes appreciable when one-tenth per cent alloys of gold are prepared, e.g., for the purpose of obtaining the standards, the one-tenthousandth, and the one-hundred-thousandth grain—in such cases special lead must be used.

Having weighed off several, say ten, portions of the necessary weight of alloy to give the desired gold prill, they are separately cupellated on small bone-ash cupels, either before the mouth blowpipe or in the muffle.

By thus heating the alloy in an oxidising atmosphere, the lead is eliminated, passing away from the gold as fused litharge, which is absorbed by the porous bone-ash of the cupel. If the blowpipe is employed a strong heat should be brought to bear upon the residual gold, so that when the flame is withdrawn, the prill remains fluid for some few seconds and has time to acquire an approximately spherical form before it solidifies. Ten such beads, if each of the thousandth of a grain or of the tenth of a m.grm., together form an appreciable weight, and can hence be together weighed to ascertain if the average weight is correct. The following is an example:—

Five portions of gold lead alloy, each calculated to contain one-hundredth of a grain (0.65 m.grm.) were cupellated; the five gold prills were detached and together weighed on an assay balance.

5 prills weighed	..	..	..	0.050 grain
Average weight of each prill	..	..	0.010	"

These beads measured (with a magnifying power that I will refer to as No. 1, and by the method later described), respectively,

21'3, 22, 21'5, 21'5, 21'5,

giving an average diameter for a bead 0.01 grain in weight of 21'5 divisions of the scale.

In a similar way were obtained the empirical measurements of prills.

0.1 and 0.05 m.grm. (0.00154 grain and 0.00077 grain); the diameters of these averaged 11.1 and 8.7 divisions.

The above standard prills are those that have been chiefly employed for the estimation of the weights of gold obtained in the experiments to be later described.

For the preparation of the standards of smaller weight, e.g., the one-tenthousandth of a grain, a gold-lead alloy containing about 0.05 per cent of gold was used, the lead being exceptionally free from silver, and obtained from litharge in the following way:—

A pound of litharge was mixed with about 5 grms. or 75 grains cream of tartar, and fused in a capacious crucible in two or three portions at a time. By this about an ounce of lead was reduced from the oxide, the residual oxide being thus partially freed from the trace of silver invariably found in the commercial litharge.

The residual litharge was pounded, again fused with the above weight of tartar, thus again separating a part

of the lead and of the trace of silver. With the remaining oxide, the partial reduction was again repeated, and, finally, after these three purifications, the rest of the oxide was mixed with excess of cream of tartar and some fine charcoal powder, and fused so as to reduce out all the lead.

To test this lead 50 grms. or 770 grains were heated on a scorifier in an oxidising atmosphere, so as to reduce the weight of metal to 10 grms. (150 grains); this, on cupellation, gave a distinct trace of silver. I therefore decided to oxidise, by scorification, two or three ounces of this fairly pure lead, collected about half an ounce of oxide (still leaving a large excess of lead in the metallic state), purified it by partial reduction, and finally fused with excess of tartar. The lead produced by this final operation was of such purity that I was enabled, by alloying it with 0.05 per cent of gold, to obtain standard prills of gold 0.0001 grain (0.0065 m.grm.), 0.00001 grain (0.00065 m.grm.), and 0.000001 (0.000065 m.grm.), perfectly free from silver, and estimated by comparison with the higher standards to be exact within an error of less than 10 per cent. In other words, the prill of gold that is now under a high power of the microscope is the millionth of a grain, and exact to the one ten-millionth of a grain. It has the colour of pure gold, is apparently perfectly spherical in form, and has a diameter, in actual measurement, according to the mean of a large number of observations, of 0.00075 inch. Assuming this minute bead of gold to be a sphere, its volume would correspond to a weight of gold equal to 0.00000107 grain.

This close agreement between the weight of the gold prill and the weight of the gold in the lead alloy taken for cupellation, proves how minute must be the loss of gold when cupellated with lead.

The average absolute diameters of the standard prills or beads have been calculated, and are given in the following Table. In the column D are given the amounts by which spheres of gold, of the specified diameters, would exceed the weights of the prills. The specific gravity of the gold has been taken as 19.2.

Weight of standard in grains.	Diameter in thousandths inch.	Relative cubes.	D. Per cent.
Hundredth	15.81	9.17	+ 0.4
Thousandth	7.55	1	+ 9
Ten-thousandth	3.63	0.110	+ 22
Hundred-thousandth	1.61	0.0097	+ 6
Millionth	0.75	0.00098	+ 7

The Measurement.—For the measurement of beads ranging in weight from the hundredth to the ten-thousandth of a grain (or from 0.05 to 0.005 m.grm.), the most convenient magnifying power is that afforded by a microscope fitted with a $\frac{1}{2}$ -inch objective and B eye-piece; although most of the results here recorded have been obtained with a one inch objective, and the microscope tube drawn out so as to give a total length of 12 inches. Some of the smaller beads (e.g., 100,000 grain) have been measured with $\frac{1}{2}$ and also $\frac{1}{4}$ inch objectives, by which the accuracy of the measurements have been greatly enhanced.

A convenient stage is one enabling a steady motion to be given to the glass slide upon which the bead is placed, so that the latter may be quickly adjusted to the scale in the eyepiece. A stage moving by rackwork is a great luxury, and enables measurements to be rapidly made.

The micrometer that I have employed is photographed down to $\frac{1}{2}$ inch from a scale ten inches long (an old thermometer scale upon white porcelain) and has about 80 divisions in the half-inch. The glass upon which the positive is taken is cut into circular form and then dropped into the eyepiece upon the diaphragm, where it is in the focus of the upper lens.* This form of micrometer is

superior to any engraved scale, being distinctly visible when the stage is illuminated, and both it and the object upon the stage can be, at the same time, brought into the focus of the eye. It is a convenience if the eyepiece fits loosely in the tube of the microscope, since then a slight turn or movement of the former can bring the apparent edge of the bead or prill, as viewed through the instrument, accurately to a unit division of the scale.

Having a gold prill (say upon the cupel), have ready a dry glass slide, plain, or having a small cell, moisten the point of a knife, gently touch the bead with it until it is loosened; the bead generally adheres to the point, and can be transferred to the glass slide. When the prills are required to be kept for reference, they may be mounted in a cell formed on the glass by gumming one or more thicknesses of paper, in which small holes have been cut, covering with a circle of glass, and fixing the latter in position by gummed paper.

The bead is lighted from below and brought into the focus of the microscope; it then appears as a black circle with well-defined edge. To measure the diameter the stage is moved until the head apparently coincides with the micrometer scale; the units, and approximately the 1-roths that the bead measures is then read upon the scale. It is well to take the measure in two directions at least, by turning the eyepiece, and with it the micrometer, through 90°; an average of the measurements is then taken.

The beads are slightly flattened at the point where they have rested upon the cupel, and, when resting upon this flattened surface appear spherical in form. Since the flattened surfaces are not always in view in taking the measurements of diameters, they are, when visible, best left out of consideration.

Knowing the measurement of a bead of standard weight, that of the prill can be calculated upon the assumption that both are approximately spherical, and therefore that the weights of the two masses are proportionate to the cubes of the diameters.

Example:—A prill of gold obtained as the result of an assay, measured under the power before recorded, 12.5 divisions.

The average diameter for 0.01 grain is 21.5 divisions, hence the weight of the prill is $21.5^3 : 12.5^3 :: 0.010 : X$

$$X = \frac{0.01 \times 12.5 \times 12.5 \times 12.5}{21.5 \times 21.5 \times 21.5} = 0.00197 \text{ grain,}$$

or approximately 0.002 grain.

If the comparison is made against the average diameter of the 0.1 m.g. beads, the weight would be estimated as 0.143 m.g., or 0.0022 grain, showing a difference in estimate of 10 per cent. I would prefer to accept the estimate made against the lower standard, since it more closely approaches in size, and therefore in form, to the assay prill. Considering, however, that this difference is in weight only 0.0002 grain, and that a balance would differ at least to 0.0005 grain in two observations, the above example will show that with the thousandth of a grain the method of measurement is superior in accuracy to that of weighing. With the aid of a table of cubes the calculations can be quickly performed.

Where the ten-thousandth of a grain of gold is to be measured, before attempting to detach the prill it is advisable (for fear of loss) to measure it while still upon the cupel. For this purpose place the cupel itself on the stage, illuminate the surface from above, focus, and measure as accurately as possible. Measurement in reflected light commonly gives a lower estimate than by illumination from below, owing to the difficulty of seeing the edges of the strongly reflecting bead. After a little practice even the 1-100,000th of a grain can be detached from the cupel and mounted in a cell. The risk of losing the prill is chiefly in detachment.

Outline on the Method of Assaying.—Taking the case of quartzose gold ores for the sake of illustration, the ore, after careful sampling and pounding into a fine state,

* Mr. Knott, of Elliott Street, Liverpool, photographed these micrometers, and can fit them to any eyepiece.

is sifted. Any metallic particles that remain on the sieve are collected and weighed. The finer ore being also weighed, proportionate parts of the two are weighed off for assay. Convenient quantities for assay are from 100 to 1000 grains, or from 10 to 100 grms., according to the richness of the ore and the degree of accuracy required in the results. By adopting the measurement system, accurate assays may be performed upon much smaller quantities than when the gold is weighed. In fact, fairly accurate and concordant assays of rich gold ores, sufficiently accurate for the purposes of a prospector, have been obtained from one grain only of material. As in all analytical tests, two or more portions should be submitted to assay. Where the method of fusion with litharge in a crucible is adopted, the weighed portions are mixed with flux, litharge, and some reducing substance, and heated to complete fusion in a good clay crucible. Convenient proportions are, in the case of quartz ore (fairly free from pyrites):—Ore, 100 parts by weight; litharge, 200 parts; soda-ash, 200 parts; and cream of tartar, 4 to 5 parts. On fusion about one-tenth or eighth of the litharge is reduced, the remaining portion serving, with the soda, as a flux for the siliceous matter of the ore. With ores containing pyrites or other sulphides, the tartar may require to be reduced in amount, or even altogether omitted, since the sulphur of the pyrites acts as a reducing agent towards the litharge. A good rule to observe is to obtain a large excess of litharge in the slag, and at most 50 parts of lead from 200 of litharge. During the fusion, the lead that forms picks out or alloys with the gold, collects at the bottom of the crucible, and there, when the ore is completely fused, receives such particles of gold that have escaped the action of the globules of lead, and that tend to fall through the fused mass of slag. To further promote the separation of the gold, a little tartar mixed with litharge may be thrown or sprinkled upon the surface of the fused mass in the crucible, so as to form minute particles of lead, which, in falling to the bottom, no doubt serve to perfect the collection of the gold. The contents of the crucible are poured into a mould, the slag again fused with a small quantity of tartar, and again poured.

The lead produced by these two operations contains, according to test experiments described later, practically all the gold of the ore,* together with the silver natural to it and to the litharge, also traces of other reducible metals, such as copper, if the ore contains such.

This alloy is heated upon bone-ash supports or cupels in an oxidising atmosphere, until all oxidisable metals are removed and absorbed as oxides by the porous bone-ash: an alloy of silver and gold is then left as a bead or globule.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

January 17th, 1890.

Prof. W. G. ADAMS, Vice-President, in the Chair.

OWING to the unavoidable absence of Mr. F. B. Hawes, his paper on "*A Carbon Deposit in a Blake Telephone Transmitter*" was postponed.

Dr. S. P. THOMPSON made a communication "*On Electric Splashes*," and illustrated his subject by beautiful experiments on the production of Lichtenberg's figures. The author has recently investigated these phenomena as modified by varying the conditions under which the figures are obtained, and has arrived at the following conclusions:—1st. The nature of the dielectric plate does

* Platinum also if present in the ore.

not change the character of the figures produced; and, 2nd, the nature of the powders used seems to have no material effect on their shape.

In the course of his experiments he has found a mixture of sublimed sulphur and lycopodium to give better figures than the red lead and sulphur usually employed, and also that a large and highly polished knob is advantageous, particularly when the Leyden jar is charged negatively. Sometimes when obtaining negative figures, nebulous patches occur, and these were attributed to the so-called electric winds sent off from roughness on the knob when not sufficiently well polished. If, instead of bringing the knob in contact with the plate, it is only brought near to it, then a peculiar figure closely resembling a "splash" results. A positive splash consists of short lines radiating from the point of approach, whilst a negative splash is made up of more or less rounded spots, which become elongated in a radial direction as the distance from the centre of the splash increases. Negative splashes are, however, much more difficult to produce than positive ones.

When viewed in the dark, the discharge producing the splash is seen to consist of a bundle of small sparks which branch outwards on approaching the plate.

In conclusion, the author remarked that roughness on a conductor produced more "electric wind" when the conductor is charged negatively than when positively charged, and invited the opinion of members as to the cause of the differences observed between positive and negative electricity.

Prof. RÜCKER said he had recently obtained figures produced by discharges on photographic plates. Generally, he observed that negative discharges produced roundish patches, whilst positive ones give more filamentary figures. On passing a spark across a glass plate covered with lamp-black, its trace was found to have a black core at one end whilst the other was quite clear. He also made remarks on the distinctive character of the positive and negative discharges in partial *vacuo*, and considered investigations as to the cause of such differences to be of great importance.

Prof. ADAMS thought any attempt to discover the cause of such differences as those noted in the paper was to be commended, for the well-known fact that it is more difficult to insulate a negative charge than a positive one has long needed an explanation.

"*A Paper on Galvanometers*." By Prof. W. E. AYRTON, F.R.S., T. MATHER, and W. E. SUMPNER, D.Sc.; read by Prof. AYRTON.

In fitting up the physical laboratories of the Central Institution of the City and Guilds of London Institute, the authors have had occasion to obtain galvanometers of various types and patterns, some of which have been made to special designs, and specimens of instruments embodying recent improvements were exhibited at the meeting.

The question as to whether fairly sensitive galvanometers should be astatic or non-astatic was answered in favour of the former system, from the fact of its being less affected by external magnetic disturbances, and the greater ease with which great sensibility may be obtained.

The usual method of placing the mirror inside the coil was shown to be undesirable, and in the newer forms of instruments Mudford's improvement of placing the mirror outside the coils has been adopted, the space near the axis of the coil being nearly filled with wire. It was also shown that if wire be wound in a certain approximately spheroidal space near the magnets, then these convolutions will tend to oppose the more distant portions of the coil; however, by winding the two parts in opposite directions, they conspire to deflect the magnet.

Details as to methods of supporting the coils were then discussed, and the importance of fitting them in boxes mounted on hinges or otherwise so as to be readily removable was pointed out.

A galvanometer devised for teaching-purposes and provided with variable damping arrangement was described, in which the damping is effected by enclosing the mirror in a glass cell whose sides can be caused to approach or recede by turning a milled head outside the instrument. This arrangement enables the damping to be varied between wide limits, and its effect on the swing produced by a given discharge can be determined. The instrument is also serviceable both as an ordinary damped galvanometer or as a fairly ballistic one.

In measuring quantities of electricity by the first swing of a galvanometer needle, a correction has usually to be introduced for damping; this correcting factor is simple enough when the damping is small, but becomes more complex as the damping increases, and to facilitate the calculations a table of values of the factor for various values of λ (the logarithmic decrement) has been calculated. From this it appears that for values of λ less than 0.5 the value of the factor is very nearly $(1 + \frac{1}{2}\lambda)$, the correction usually employed.

Improvements in methods of insulating the coils and terminals of galvanometers required for insulation tests were next described, the principle of which may be gathered from Figs. 107 and 108 in Prof. Ayrton's "Practical Electricity." A special form of instrument for high insulation work was exhibited, in which the copper resistance of the coils is nearly 400,000 ohms, and the shortest path along which surface leakage can take place from the coils to the base of the instrument is between 30 and 40 inches of ebonite artificially dried by sulphuric acid. This is attained by supporting the coils from two corrugated ebonite rods which depend from a brass ring carried on the top of three corrugated pillars fixed to the base plate. The instrument was constructed to drawing and specification by Messrs. Nalden Bros., but the method of supporting the coils was suggested by Messrs. Eidsforth and Mudford.

With reference to the proportionality of deflection to current in reflecting galvanometers, it was pointed out that ordinary instruments may differ as much as 2 per cent within the limits of the scale, hence showing the necessity for calibration when any approach to accuracy is desired. Galvanometers, of the D'Arsonval type sometimes differ from proportionality quite as much as the one above referred to, but by fitting such instruments with curved pole-pieces, and allowing the coil to hang freely from the top suspension, a proportionality true to less than 0.15 per cent has been attained over a scale about 30 inches long.

Coming to the question of sensitiveness, the importance of keeping the wire as close as possible to the magnets was brought prominently forward, as well as the necessity of reducing the "figures of merit" of various instruments to the same standard in comparing their sensitibilities. The standard adopted as most convenient, and closely approximating to practical usage, is arrived at by supposing the distance of the mirror from the scale to be equal to 2000 scale divisions, and the sensitibilities for current and quantity are given as *scale divisions per micro-ampère*, and *scale divisions per micro-coulomb* respectively. The period of oscillation is also taken into account.

A table showing the resistances, sensitibilities, coefficients of self-induction, and volumes of the coils of various instruments, together with the relations existing between them, accompanies the paper, and from this it appears that in the best astatic coil instruments of from 10,000 to 30,000 ohms resistance, the number of scale divisions per micro-ampère may reach 400 times the resistance to the 3th power ($400 R^{\frac{1}{3}}$) when the period is ten seconds.

In obtaining data of various instruments the authors have consulted, amongst others, Prof. Threlfall's paper on the "Measurement of High Specific Resistances," in the *Phil. Mag.* for Dec., 1889, and noticed two serious errors. The first of these makes an instrument constructed according to Messrs. Gray's pattern nine times less

sensitive than it actually was, whilst the sensibility of a form recommended in the paper is given seventeen times too great.

On account of the lateness of the hour the discussion was adjourned till Feb. 6, before which time it is hoped that a fairly full abstract will appear in the technical papers.

NOTICES OF BOOKS.

A Practical Treatise on the Manufacture of Vinegar and Acetates; Cider and Fruit Wines; Preservation of Fruits and Vegetables by Canning and Evaporation; Preparation of Fruit-Butters, Jellies, Marmalades, Catchups, Pickles, Mustards, &c. Edited from various sources by WILLIAM T. BRANN. Illustrated by Seventy-nine Engravings. Philadelphia: H. C. Baird and Co. London: Sampson Low, Marston, Searle, and Rivingtons, Limited.

WE have here a work which may be pronounced more comprehensive and more trustworthy than any other on the subject in the English language. The author does not give a mere collection of recipes; he endeavours, and successfully, to place the manufacture of vinegar upon a rational basis. The work commences with a history of vinegar, in which we are sorry to find the myth of Hannibal dissolving rocks by means of vinegar. The manufacture of vinegar from alcohol will, he considers, become increasingly difficult, on account of the price of raw material and of the growing competition of wood-vinegars, which are now obtained free from the trace of tar products. Still, absolutely pure acetic acid has never the aroma of alcohol- and fruit-vinegars, due of course to ethereal compounds. We have never met with a specimen of malt vinegar—so much admired in England—which possessed anything approaching the bouquet of wine-, sugar-, and cider-vinegars. This, of course, is not a point which can be decided analytically.

As regards the theory of the formation of vinegar, the successive results of Doberiner, Liebig, Pasteur, and Nägeli are duly noticed. A curious fact here mentioned is the occurrence of acetic acid in the mineral waters of Bruckenau and in a river of Brazil. In summing up the principles of the manufacture he shows that all saccharine plant juices are suitable for the production of vinegar, and that specially prepared mixtures of water and alcohol must contain small proportions of organic substances and of salts.

The optimum temperature for the manufacture of vinegar is 86° F. within the generator, though the air outside must be kept cool. That the best modern processes are still defective is shown by the fact that the average loss due to evaporation, excessive oxidation, &c., is from 15 to 20 per cent, and that in some cases it reaches 30 per cent.

The best method of operation requires to be modified to suit the nature of the materials employed. Potato spirit, it is remarked, being contaminated with fusel, yields a vinegar of unpleasant smell. Beer vinegars are, of course, spoiled by the presence of the hop, the bitter principle of which is not eliminated. It is even questionable whether the comparatively dull flat taste of malt-vinegars is not mainly due to the presence of dextrin and other extractive matters opposing etherification.

In the vinegar manufacture the author states that irregularities and disturbed actions are more frequent than in any other industry based upon fermentation. Among the chief kinds of mischief are the "sliming" of the generators, especially frequent if too much carbohydrate is present. Vinegar-eels, vinegar-mites, and vinegar-flies are also at times very troublesome, and the most scrupulous cleanliness is required to prevent their

multiplication. Sulphurous acid kills the eels, but if used in large quantities it is also fatal to the ferment, in which case the generators have to be carefully washed out and charged again.

Fruit vinegars, e.g., the American cider vinegar, possess a delicious flavour, but they frequently do not keep well. We believe such vinegars are not made in England upon a commercial scale, though they might probably furnish a remunerative means of utilising apples and small fruits when the markets are glutted.

The vinegar from sugar-beets is quite unfit for use on account of its bad odour and flavour.

Instructions are given for preparing vinegars and vinous fluids from a variety of fruits.

A succeeding chapter enters into the manufacture of "vinegar specialities," i.e., toilet vinegars, table vinegars, such as those of aniseed, anchovies, tarragon (simple and compound), herb, pineapple, celery, and lovage vinegars, &c.

The ravages of the phylloxera have greatly interfered with the production of wine vinegars. It appears that fine wine vinegars can be obtained only by the slow process, the quick process yielding a product lacking bouquet.

The preparation of wine vinegar from lees is an important branch which might be profitably extended.

Next follow a variety of analytical procedures useful to vinegar manufacturers, such as the determination of sugar in the mashies or extracts, the estimation of the alcohol by various methods, and that of acetic acid. An important matter is the detection of extraneous acids and of metals in vinegars.

There are also instructions for ascertaining the derivation of a vinegar. Grain (beer and malt) vinegars are recognised by the presence of phosphoric acid, and by the residue of carbonised dextrin which they leave on evaporation. Wine vinegars are characterised by the presence of potassium bitartrate, which, however, is sometimes fraudulently added to spurious vinegars.

Passing over the manufacture of wood-vinegar, the preparation of commercial acetic acid, and of the acetates, we come to the manufacture of ciders and fruit wines. Very useful tables are here given of the proportions of sugar, of free acid, and of the proportion between acid, sugar, pectine, gum, &c., contained in various fruits and their juices. We may here suggest the propriety of confining the name grape-sugar to that naturally present in fruits, whilst glucose should denote the artificial product.

Various compound ciders are here mentioned, some of which might be usefully made in England.

The author speaks, curiously enough, of "pear cider," a liquor which in this country is always called "perry."

In speaking of "rhubarb wine" Mr. Brannet does not mention that it can scarcely be free from oxalic acid.

The preservation of fruit with a variety of accessory processes is next considered. Here we find it stated that both plums and cherries are comparatively dear in the United States, in part, perhaps, from the climate and in part from the ravages of insect enemies. As regards the solder used in making up tins of fruit, it should be mentioned that zinc chloride, a most formidable poison, is used by the plumbers in place of resin, as being cheaper and easier of application.

This work deserves to be warmly recommended, not merely to vinegar manufacturers, but also to farmers, fruit-growers, pickle-makers, and all persons concerned in the utilisation of vegetable products.

A Handbook of Quantitative Analysis. By JOHN MILLS (of the Normal School of Science) and BARKER NORTH (Associate of the Normal School of Science). London: Chapman and Hall, Limited.

WITH two reservations, this work merits general approval. The first of these excepted points is that it is openly and avowedly examinational in its aims, being written "to

meet the requirements of students entering for" certain examinations duly specified. The second point is that there already exist works conveying instructions for the performance of all the operations here given. There are directions for organic analysis, the nitrogen being determined by the processes of Dumas and of Will and Varrentrap. The Kjeldahl process is not mentioned. Gas analysis very properly forms the subject-matter of a chapter. The instructions for water analysis are substantially based upon the Wanklyn and Chapman manual. No reference is made to the estimation of organic nitrogen by the Frankland process, which has been generally supposed to be an article of the faith at South Kensington. Nor is there any notice of the permanganate process, which in its present improved state is not without value. There is a brief account of the determination of the precious metals by cupellation.

The chapter allotted to the analysis of commercial products makes mention only of bleaching-powder, porcelain, gunpowder, white-lead, sugar, soap, and iron in its different forms. We scarcely think that gunpowder or porcelain often come under the hands of the analyst.

Quinine as a Prophylactic or Preventative against Malaria Fever.

THIS pamphlet, which is compiled by Messrs. C. F. Boehringer and Sons, of Waldhof, near Mannheim, does not bear the name of any publisher or printer. The eminent medical authorities recommend that quinine, in combatting malarial fever, should be used in large doses — 1 grm. or upwards — and preferably not as sulphate, but as the more soluble hydrochlorate dissolved in dilute alcohol. Sailors arriving at the very unhealthy port of Tandjong Priok in Java received the first day each 1 grm. of quinine dissolved in gin, repeating the dose on the 8th, 12th, and 16th days, and on the 10th and 14th days $\frac{1}{2}$ grm. Other authorities shorten the interval between the first and the second dose, but all agree that ordinary doses are useless for combatting the malaria of tropical climates. Schweinfurt whilst botanising in the African swamps took $\frac{1}{2}$ grm. three times daily. Stanley took doses of 3 and $3\frac{1}{2}$ grms.

CORRESPONDENCE.

THE POSITION OF THE CHEMIST.

To the Editor of the Chemical News.

SIR,—The CHEMICAL NEWS (vol. lxi., p. 26) contained an advertisement for a "Gas Examiner," to be appointed "in accordance with Sect. 27 of the Metropolitan Gas Act, 1860, at a salary of £25 per annum. The person appointed must provide, at his own expense, a place suitable for gas-testing within the district, but all necessary apparatus for so doing will be provided by the Board."

These terms throw an interesting light on the estimation in which our municipal authorities hold a professional chemist. For the magnificent sum of £25 the grateful recipient is to "provide at his own expense a place suitable for gas-testing," and do the work.

If the latter is aught but a sham it means, say, two hours per day on three hundred days per annum; or six hundred hours' work. If the "suitable place" is obtained for a rent of £5 per annum, then 8d. per hour is the munificent wage of the tester.

Why, sir, even that long-suffering down-trodden creature, the gas-stoker, would have enough of the worm in him to turn at such an offer as this. Did not the docker triumphantly assert his claim to a minimum wage of 2s. for casual employment not exceeding four hours per day? The casual chemist is only to have two hours, however, and be paid only 1s. 4d.

Sir Henry Roscoe, in a recent speech, is reported by *Nature* to have admitted that we "have yet to create a demand for technically instructed persons." True, O King! And yet this has been forgotten, and all our energies are devoted to creating not a demand, but a supply.

What a happy time is in store for the pupils, and still more for the staffs of our various technical schools, now so anxiously pushing their wares on the world's market.—I am, &c.,

R. J. FRISWELL.

Atlas Works, N.E., Jan. 15, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 1, January 6, 1890.

Certain New Fluorescences.—Lecoq de Boisbaudran.—The author has obtained certain fluorescences by taking as active matters samaria and the earths Za and $Z\beta$, and as solid solvents calcined silica and zirconia. He indicates here merely the chief spectral positions.

The Refracting Powers of Simple Salts in Solution.—E. Doumer.—The author's results lead to the following conclusions:—(1) All the salts formed by one and the same acid have the same molecular refractive power when they are formed on one and the same type. (2) The refractive powers of salts belonging to different types are sensibly multiples of a common number. (3) The molecular refringent powers of salts are functions of the number of valencies of the metallic element which enters into their composition. These observations lead to the novel notion of *masses optically equivalent*.

Composition of the Rocks employed in the Manufacture of Porcelain in China.—Georges Vogt.—The Chinese minerals are very different in composition from those used for the same purpose in Europe. Their kaolins differ little from those of Europe, but the yeou-ko and the petun-tse differ decidedly from pegmatite by containing white mica (muscovite). This mineral is met with in Chinese porcelain slip to an extent often bordering on 20 per cent.

On Matezite and Matezo-Dambosé.—Charles Combes.—A. Girard has extracted from the juice of the caoutchouc of Madagascar a sugar which he called matezite, which, on treatment with hydriodic acid was split up into methyl iodide, and a sugar, matero-dambosé, an isomer of the glucoses. The author now finds matezite identical with β -pinite and matezo-dambosé identical with β -inosite.

The Carballylates.—E. Guinochet.—The carballylates much resemble the aconitates, but they are distinguished by the following point:—The solutions of the tribasic carballylates are neutral to litmus and phenolphthalein, whilst the corresponding aconitates are alkaline.

Moniteur Scientifique, Quesneville.
December, 1889.

Notice of the late Dr. Gustave Augustin Quesneville.—The late Dr. G. A. Quesneville was born at Paris, January 1, 1810. His father, J. B. J. Quesneville, had succeeded Vauquelin in the manufactory of chemical products founded by that eminent *savant*. In 1823 Liebig executed here his first great research, the investigation of the fulminates. Shortly before the revolution of 1830 Quesneville had been appointed a professor at the courses instituted at the Tuileries. He was also for some time

assistant to Chevreul. In 1834 he graduated as Doctor of Medicine, and practised for two years as a physician. He then returned to chemistry and occupied himself with the manufacture of chemical products. As far back as 1826, at the age of sixteen years, Quesneville published his first discovery, a method for the separation of iron from manganese by precipitation with potassium arseniate. Among his subsequent results were the preparation of barium dioxide, a method for obtaining cobalt oxide in a state of approximate purity, a process for the production of volatile chlorides, and a method for obtaining uranium oxide without the use of ammonium carbonate. In investigating the composition of urinary calculi he discovered that facitious specimens had been made up of calcium carbonate and phosphate cemented together with bread paste! His studies on hydrogen peroxide seem to have been generally forgotten and re-discovered. His pharmaceutical improvements and discoveries were both numerous and important. Dr. Quesneville had, above all things, an independent spirit; not anxious to please the scientific powers of the day, whose occasional acts of injustice he was always ready to expose. On the other hand, he loved to encourage discoverers who combated on behalf of some novel truth. Thus, he participated in that revolution in organic chemistry of which Gerhardt and Laurent were the promoters. We have the pleasure of announcing that the *Moniteur Scientifique* will be continued by M. Georges Quesneville, the son of the late editor.

Notes on Colouring-Matters at the Exhibition of 1889.—It is remarked that this industry has made less progress since 1878 than it has done in the eleven years previous. The results comprise the application of more scientific methods to the older manufactures, and the addition of a great number of representatives to series already known. The display in this department would have been more extensive had it not been for the entire abstention of Germany and—save for a single firm—that of Switzerland.

Study on Morphine.—L. Knorr.—The author concludes that morphia is a tertiary base containing a methyl united to nitrogen. In methocodeine there are two methyls combined with nitrogen. In consequence we may explain the transformation of codeine into methocodeine by the rupture of a closed chain, in which the nitrogen of the morphine is included. This hypothesis agrees with the fact that under the same circumstances we may add to methocodeine two atoms of bromine more than to codeine. Morphine contains a phenanthrenic nucleus which, in reason of the high proportion of carbon in morphine, may be reduced in part. Metho-codeine treated with acetic anhydride is decomposed into β -oxyethylidimethylamine and into a phenanthrenic derivative. Morphine contains a phenolic hydroxyl, an alcoholic hydroxyl, and a third indifferent oxygen, which probably serves as connecting link. The alcoholic hydroxyl of morphia retains its character in metho-codeine, and only appears as phenolic hydroxyl after the decomposition of the methocodeine into acetyl-methylidioxphenanthrene.

Syntheses in the Series of the Oxazines.—L. Knorr.—The author describes the synthesis of methylmorpholine, of phenylmorpholine, of phenomorpholine, and of α -methylphenomorpholine.

Purification of Arseniferous Sulphuric Acid.—Professor Kupferschläger. The author dilutes the acid with an equal weight of distilled water, passes through it a current of washed sulphurous acid, and then, in two repetitions, a current of washed sulphuretted hydrogen. The purified acid is then rectified.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—A crystallographical paper, incapable of useful abstraction.

Industrial Society of Mulhouse.—Session of Oct. 9, 1889.—M. Matthieu Plessy sends in a note on a new re-

agent for cane-sugar, grape-sugar, and pyrogallie acid. It is a solution of lead parnitrate, NO_4PbH , in an excess of melted ammonium nitrate.

Session of Nov. 13, 1889.—M. Cordillot describes a process of continuous steaming practised since 1874. The apparatus is composed of a large iron chamber in which there are six wagons in which the pieces are successively heaped up.

M. Boeringer [sent in a paper on improvements in printing by hand. The use of gum tragacanth enables the deepest colours to be printed over the lightest.

Aniline Black and the Grawitz Processes.—Opinions on the validity of Grawitz patents.

Patents concerning Colouring-Matters.—A series of specifications of chemical patents.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 47.

Extraction of Glycerin in Soap Works.—This paper is taken from English sources, and gives an account of a process used by Matison and Co., of Widnes.

MISCELLANEOUS.

Central Institution, Exhibition Road.—Mr. Holland Crompton will deliver a special Course of Ten Lectures (commencing Jan. 24, at 4.30 p.m.) on the Theory of Electrolysis and the Nature of Chemical Change in Solution, in which the recent development of the Clausius dissociation hypothesis of electrolysis will be fully discussed. Prof. Armstrong will deliver a special Course of Ten Lectures (commencing Jan. 27, at 4.30 p.m.) on Methods of Analysis as Applied to the Determination of the Constitution of Carbon Compounds, dealing with the more important and typical compounds, including alkaloids, carbohydrates, oils, and fats.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Medical, 8.30.

Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.

TUESDAY, 28th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.

Institute of Civil Engineers, 8.

Royal Medical and Chirurgical, 8.30.

Society of Arts, 8. "The Relation of the Fine Arts to the Applied Arts," by Edward C. Robins, F.S.A.

WEDNESDAY, 29th.—Society of Arts, 8. "The Utilisation of Blast-furnace Slag," by Gilbert Redgrave.

THURSDAY, 30th.—Royal, 4.30.

Royal Institution, 3. "Sculpture in Relation to the Age," by Edwin Roscoe Mullins.

FRIDAY, 31st.—Royal Institution, 9. "Smokeless Explosives," by Sir Frederick Abel, C.B., D.C.L., D.Sc., F.R.S.

SATURDAY, Feb. 1st.—Royal Institution, 3. "The Natural History of the Horse, and of its Extinct and Existing Allies," by Prof. Flower, F.R.S., &c.

CITY AND GUILDS OF LONDON INSTITUTE
FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.

CENTRAL INSTITUTION, EXHIBITION ROAD, S.W.

A Course of Ten Lectures on Methods of Analysis as Applied to the Constitution of Carbon Compounds will be delivered by PROF. H. E. ARMSTRONG, F.R.S., on Monday, at 4.30 P.M., commencing January 27.

Mr. HOLLAND CROMPTON will deliver a Course of Ten Lectures on the Theory of Electrolysis and the Nature of Chemical Change in Solution on Fridays at 4.30 P.M., commencing January 24. Fee for each Course, 10s.

Particulars of and tickets for the Courses may be obtained on application to the Dean, Central Institution, Exhibition Road, S.W.

JOHN WATNEY,
WALTER S. PRIDEAUX, } Hon. Secs.

A. I.C., 22, speaking fluently French, German, and Danish, Assistant in Mineral and Agricultural Laboratory of Prof. Hof. R. Fresenius, Wiesbaden, desires situation in Manure or other Works; home or abroad.—Address E Woodward, 57, Rheinstrasse, Wiesbaden.

A Gentleman (age 40) holding Advanced Science and Art Certificates in the following subjects wishes for appointment:—Mathematics (Second Stage); Sound, Light, and Heat; Electricity and Magnetism; Inorganic Chemistry; Organic Chemistry (Hof.); Geology; Human Physiology; Botany; Biology; Metallurgy; Steam and Applied Mechanics; National Medallist in Physiology; Trained in Chemistry, Physics, and Biology at Normal School of Science, London. Good Demonstrator and Lecturer.—Address, "Science," CHEMICAL NEWS Office, Boy Court, Ludgate Hill London, E.C.

A large Soda Manufactory in Germany, working after the Ammonia Process, seeks a thoroughly experienced and self-dependent Manager who is well acquainted with the process, having worked already in a self-dependent position in similar manufactories, and must be able to give sufficient guarantees for a lucrative working.—Apply, stating salary expected and enclosing testimonials or references, to H 5384, care of Haasenstein and Vogler, A. G., Frankfurt-on-the-Main.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive Tenders for the supply of 2000 tons of MANGANATE OF SODA, to be delivered at the rate of not less than 100 nor more than 200 tons per week from April 1, 1890.

Persons tendering will be required to declare in their Tender that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council, at the Office, Spring Gardens, until Monday, February 17, 1890. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., must be endorsed "Tender for Manganate," and be sent in not later than 10 o'clock on Tuesday morning, the 18th of February next.

The Council does not bind itself to accept the lowest or any Tender.

Spring Gardens, S.W.,
January 21, 1890.

H. DE LA HOOKE,
Clerk of the Council.

The Valuable and Complete CHEMICAL

MANURE WORKS, known as The Silvertown Chemical Works, Silvertown, for SALE.—The premises have been constructed at considerable cost for the purpose of a very large trade, and the machinery is complete in every respect for the immediate carrying on of the business; there is a wharf with a frontage of about 100 feet to the River Thames, so that all goods can be loaded and unloaded direct from the wharf, also a railway siding connecting the works with the various railway systems of the United Kingdom; the premises comprise spacious manufacturing, storage, and packing works, pyrites burners, acid chambers capable of producing 5000 tons chamber acid per annum, office, laboratory, and caretaker's house; the plant is capable of producing 20,000 tons of manure per annum, which could, at a small outlay, be greatly increased; all parts of works are connected by tram lines.—For particulars apply to Walter W. Feast, Esq., Chartered Accountant, St. George's House, Eastcheap, London, E.C.; or to Messrs. Hatchett, Jones, and Co., Solicitors, 47, Mark Lane, London, E.C.

ALKALI MAKERS' PLANT AND MACHINERY.

FOR SALE, by Private Treaty, at the Jarrow Chemical Company's Tyne Dock Works, South Shields, a large quantity of ACID, ALKALI, and CAUSTIC SODA PLANT, in good condition, which may be viewed at any time.—Apply to the Jarrow Chemical Co., Limited, Tyne Dock, South Shields.

Magnesit, Raw, 2s. 6d. per 2 cwt.; in powder, 4s.; also burnt and slightly burnt Magnesia, Silver-polish, Mineral Pumice-stone of every kind, Magnesia Powder, Tripoli of every kind, Polishing Chalk, Emery Powder, Polishing Powder, Spathe of every kind, Slate Powder of every kind, Asbestos Slate Powder, Magnesia Mari, cheap from BRÜCK'S GRUBEN COMPTOIR, Berlin, S.O.

Water-Glass, or Soluble Silicates of Soda and Potash, in large or small quantities, and either solid or in solution, at ROBERT RUMNEY'S, Ardwick Chemical Works, Manchester

FOR SALE.—THE CHEMICAL GAZETTE. Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," CHEMICAL NEWS Office, Boy Court, Ludgate Hill London, E.C.

THE CHEMICAL NEWS.

VOL. LXI. No. 1575.

ON THE GENESIS OF ELEMENTS.

By H. M. VERNON.

SINCE the time when Prout first formulated his hypothesis of the genesis of the elements from the primordial atom, there has always been a feeling in the minds of chemists that this hypothesis may possibly in some future time be verified experimentally, at least to a certain degree. This feeling has been strengthened during the last few years by the discoveries of Crookes and other chemists, of what have been termed the meta-elements. Crookes, starting from a specimen of mineral supposed to contain only one or two rare earths, has succeeded by a laborious process of fractionation in resolving one of these earths, supposed to be the oxide of a single element, into several other earths, all of which have properties almost exactly similar, and only capable of being distinguished in some cases by the difference in their colours or by the difference of a single line in their spectra. These earths are the oxides of elements of scarcely perceptibly different atomic weights, for all of which it would not seem possible to provide a place in the table of elements arranged according to Mendeleeff's Periodic Law.

Arguing from these discoveries, Crookes asks whether it may not be possible by suitable methods of fractionation to separate many, if not all, of the rest of the so-called elements into a number of other elements almost exactly similar in properties and in atomic weights, and thus to obtain an almost infinite series of elements, the properties of which gradually change in regular order as they pass through the cycles of the series of elements arranged according to the periodic law.

Many almost insurmountable difficulties, which it will be unnecessary to enumerate, have been brought against this chain of reasoning by various chemists. This hypothesis, being for the present, at least, therefore considered unacceptable, we come to the question as to whether there is no other hypothesis that has the same end in view which is capable of being formulated, such that may appeal more readily to the minds of chemists. It is with this object in view that these few ideas have been brought forward.

At the beginning of the universe we may consider it very probable that there existed only the primordial atom, which, as in the course of ages, became gradually cooled down, united amongst itself to form the complete cycle of elements as known to us at the present day. Those elements most stable as regards heat would first be formed as this process of cooling went on, while those least stable with regard to heat would be formed last, all elements but the first being formed by the addition of other primordial atoms to the elements already formed.

If this be the case we may conversely regard it possible to disintegrate some at least of the so-called elements into bodies more simple than themselves, that is, into bodies more stable as regards heat, by heating them to a sufficiently high temperature. If, indeed, a high enough temperature could be obtained, it would be possible to disintegrate all the elements known to us into not only simpler bodies than themselves, but into the primordial atom from which all the elements were originally formed.

The question now comes whether it will be possible to obtain the extremely high temperature necessary for this purpose. The reply is that, as far as can be seen, there is no possibility of ever reaching a temperature high enough to decompose an element into its primordial atoms; but that it may be possible to reach a temperature high

enough at least to decompose some of the elements least stable as regards heat into bodies more stable with regard to heat than themselves.

The reason for this reply is that the only practicable means we have for obtaining high degrees of temperature are (1) utilising the heat evolved by the combination of bodies with each other and (2) by means of electricity.

It is obvious that only a certain degree of temperature can be obtained by the first method, as the compounds formed by the combination would be incapable of existing above this temperature, and therefore no combination would take place, as there would be no affinity between the bodies.

In the case of electricity also, as far as may be judged, it is only possible to obtain a certain degree of temperature. We may therefore ask whether it is not possible by any other means than direct experiment to ascertain whether so-called elements cannot be decomposed into bodies simpler than themselves by the action of heat.

By means of the spectroscope it has been found possible to ascertain the presence of many of the elements in the sun, and to a certain extent those present in the fixed stars.

The temperature of the sun is admittedly very high. Is it not possible that it is high enough to have caused some of our least stable elements to have been disintegrated into more simple bodies?

Of the elements known to us, about half have up to the present been shown by Thalén, Lockyer, and others to exist with more or less probability in the sun. The proofs of the presence of some of these elements depend upon the coincidence of only a very few lines of the sun's spectrum with those of their spectra as known to us; their presence may, however, be provisionally accepted.

If these elements be arranged in order of their atomic weights according to Mendeleeff's Periodic Law, the places of the elements whose presence in the sun has not been proved being left as blanks, we obtain the following table:—

Groups.	1.	2.	3.	4.	5.	6.	7.	8.
1.	H							
2.	Li	Be						
3.	Na	Mg	Al					
4.	K	Ca	—	Ti	V	Cr	Mn	Fe Co Ni
5.	Cu	Zn	—	—	—	—	—	—
6.	Rb	Sr	Y	—	—	Mo	—	Ru Pd
7.	Ag	Cd	In	Sn	—	—	—	—
8.	Cs	Ba	Ce	La	—	—	—	—
9.	—	—	Er	—	—	—	Ir	Pt
10.	—	—	—	Pb	Bi	—	—	—
11.	—	—	—	—	—	U	—	—

From this table we see that almost all the most positive elements are present, but that as the elements become more and more negative, fewer and fewer appear capable of existing in the sun's photosphere. Thus no less than eight of the elements occurring in the first group and seven of those in the second group have been shown to be present. When, however, we come to the third group, in which the elements are of a more negative character, their instability with regard to heat becomes more marked, only five of them being found to be present. Only four of the elements of the fourth group are found to be present, and of the fifth group only two; of the sixth group three elements apparently are present, while of the seventh group manganese is the solitary representative. The eighth or extra group of the table is very well represented, probably seven, if not more, of the elements occurring in this group being present. Of these elements, too, iron and nickel occur in the sun in quantities as great as almost any other element. The behaviour of this group is therefore abnormal in very much the same way as it is in the arrangement of elements according to the periodic law.

We therefore find with striking regularity that as we

proceed from the left hand group of positive elements to the right hand group of negative elements in Mendeleeff's table, the number of elements of each group found to exist in the sun's photosphere decreases proportionately to the increase of negative properties of the elements of each group taken as a whole.

If, now, it be granted that the majority, at any rate, of the other known elements are not present because they are decomposed by the high temperature of the sun into bodies simpler (that is, more stable with regard to heat) than themselves, we find, as a rule of general applicability, "that as we pass from positive to negative elements the stability of the elements with regard to heat decreases proportionately as their negativity increases."

We see from the above table that it is not merely that non-metallic elements taken as a whole are less stable with regard to heat than metals, but that elements, whether metals or non-metals, are stable with regard to heat or the reverse according to their positivity.

The fact that no non-metallic elements appear in the table, unless we except hydrogen, would show that these bodies taken as a whole are much less stable with regard to heat than the metals. This is quite borne out by what is otherwise known of their behaviour when subjected to moderately high temperatures. Thus almost all the non-metallic elements which have been volatilised have been found to possess simpler molecules at higher than at lower temperatures. The molecule of sulphur at 450° C. contains six atoms, while at 800° C. it contains only two. At a still higher temperature it would probably contain only one.

Phosphorus and arsenic at a red heat contain four atoms in their molecules, while at a white heat they contain only two. Up to moderately high temperatures the molecules of bromine and iodine contain two atoms, but at 800° the molecule of bromine and at 1500° the molecule of iodine contain only one atom. At a still higher temperature chlorine would probably act in a similar manner. Even in the case of the non-metals carbon, boron, and silicon, which have not been volatilised, it has been shown by Weber with a considerable amount of certainty that the constitution of these elements is much more complex at lower than at higher temperatures. This follows from the fact of their specific heats being very much greater at higher than at lower temperatures; thus the specific heat of the diamond at 985° C. is about seven times greater than it is at -50° , so probably the molecule of diamond at a temperature slightly below this contains eight times as many atoms as the molecule at 985° C. Very much the same thing will hold in the case of boron and silicon. If, then, as is shown by these facts, the molecules of the non-metallic elements are more simple at higher than at lower temperatures, it would seem very probable that at higher temperatures still their constitution would become still more simple, that is, they would be split up into other bodies, which bodies might very possibly be some of the more stable elements at present known to us.

When we examine the constitution of the gaseous molecules of some of the metals we find their behaviour to be totally different from that of the non-metals. The molecules of all the metallic elements at present examined are found to contain one atom and one atom only, whatever be the temperature to which they are subjected. The metals which have been examined so far are sodium, potassium, zinc, cadmium, and mercury. All these elements, except mercury, have been found to exist in the sun, and it has not been conclusively proved that this element is not present.

If the vapour densities of other metals were taken it would very probably be found that at all temperatures the molecules of the more positive metals contained only one atom, but that as they began to develop negative properties their molecules would be more complex at lower than at higher temperatures, thus indicating that at higher temperatures still, such as that of the sun, they

would probably dissociate into still more simple bodies, that is, that they would cease to exist in the form of the original elements, but would be changed to some other bodies more stable with regard to heat.

At a temperature still higher than that of the sun, it would be reasonable to suppose that a still smaller number of elements would be capable of existing as such. As a proof of this supposition, it has been shown by Huggins and others that the constitution of the white, and therefore presumably hottest, stars is exceedingly simple, their spectra containing only a few lines, and therefore showing the presence of only a very few different kinds of matter.

From the above result may we not conclude that there is a possibility, if not a likelihood, of our arriving at some knowledge of the genesis of elements by endeavouring more exactly to ascertain the temperature of the sun and the elements forming it, and also by endeavouring to split up some of the least stable of the elements, as known to us, by the action of heat. If it were possible to ascertain the variations in the temperature of the sun at different points of its photosphere and chromosphere (and it is very probable that it varies enormously), and also the composition of the vapours at these points, it might be possible to arrive at a rough conclusion as to the elements which were capable of existing as such at various temperatures and those which were not.

ESTIMATION OF FATTY ACIDS IN ALIZARIN OIL.

By FRED. GUTHRIE.

ABOUT 5 grms. of the oil are weighed out in a small beaker and washed with a little water into a 6 oz. flask, 10 c.c. of normal caustic soda added, and the contents boiled slowly for half an hour. 20 c.c. of normal sulphuric acid are now added, and the flask heated on a water-bath for half an hour or more; the contents of the flask are then transferred to a tared Swedish filter, the flask shaken vigorously several times with boiling water, and the contents each time being added to the filter. The fatty acids are washed with boiling water till free from acid, the filter and fat transferred to a tared platinum capsule and dried at 212° for eight hours or till constant. The advantages of this process are threefold:—

1. The sulpho-fatty acids are decomposed, the sulphuric acid washed away; therefore the fatty acids do not blacken and decompose on drying at 212° F.

2. The fatty acids are practically insoluble in boiling water, and can be washed well from the acid used to liberate them.

3. Any free oil which the alizarin oil may contain will be saponified and weighed as fatty acid.

NOTE.—In exact estimations it is well to dry the small flask in which the fatty acids were liberated, and to wash it out with a little ether into a small beaker, the ether boiled off, and any fat left weighed.

Birchvale Print Works,
VIA Stockport, Jan. 21, 1890.

ON COOLED FLAMES.

By Dr. L. C. LEVOIR, Delft, Holland.

WHEN a small semi-globular iron spoon is held with the plane of the orifice nearly vertical to the flame of a Bunsen burner, and a very small quantity of arsenic is in it, then the flame directly appears bluish; even very small quantities of arsenic show that colour.

When Fletcher's compound blowpipe (List No. 160 May, 1889, p. 76), or what is also called a Maugham-

Burner, is used, and air is not admitted, then arsenic gives no colour, and at three feet above the burner no smell is perceived. But as soon as blowing begins a peculiar smell is perceived at three feet above the flame, which shows that unburned hydrocarbons escape from it. Evidently the temperature of the flame is lowered by the excess of cold air. These flames are very sensitive for elements of different volatility.

Arsenic shows its colour before potash or soda.

This experiment and its explanation show that it is not good in coal-gas stoves to cool the flames by pumice or asbestos bundles, as hydrocarbons which might have given heat escape unburned by their cooling influence.

When splinters of wood boiled in water with arsenious acid are held against the tube of a Bunsen burner it is possible to cool their flames to such a degree that neither luminous hydrocarbon flames nor flames coloured by the potash and soda from the ash can be perceived.

In that way I believe that cooled flames may become a fruitful field in qualitative analysis.

SEPARATION OF BARIUM AND STRONTIUM.

By R. FRESENIUS.

For the separation of barium and strontium, independently of indirect methods the following processes have been proposed and tried:—

1. Separation depending on the different behaviour of the sulphates in alkaline carbonates.
2. Separation by hydrofluosilicic acid.
3. Separation by chromic acid.

The two former methods have, for a long time, been neglected, or only very imperfectly elaborated; for, although P. Schweitzer ("Catalogue of the University of the State of Michigan," 1876, Part 1) undertook very thorough studies on the determination of barium as sulphate, carbonate, chromate, and oxalate, as also its conversion into silicofluoride, as well as on the determination of strontium as sulphate, the research does not seem to have extended to the separation of the bases.

The separation of the bases by means of chromic acid has certainly been discussed in a series of memoirs, but the results of experiments vary greatly, so that the method is recommended by many as good, but rejected by others as worthless. Hence it seems advisable to submit the question to a new critical scrutiny.

1. Separation founded on the Different Behaviour of Barium and Strontium Sulphates with Alkaline Carbonates.

H. Rose founded a process for the separation of both bases upon the fact (ascertained by himself) that strontium sulphate, even at common temperatures, is gradually but completely converted into strontium carbonate by a solution of ammonium carbonate, whilst barium sulphate, on similar treatment, remains unaltered. If the conversion of strontium sulphate is to be effected rapidly, Rose recommends that the sulphates should be boiled with a solution of potassium carbonate to which a third, or rather more, of potassium sulphate has been added, boiling for about ten minutes.

Rose gives the preference to this method of separation.

To this process P. Schweitzer objects, saying that barium sulphate, though when existing alone it is not affected by ammonium carbonate, is converted into barium carbonate if it co-exists with strontium sulphate in large quantity. On the other hand, strontium sulphate, if existing alone, is readily converted by ammonium carbonate, but undergoes no change if it is mixed with much barium sulphate.

These communications by Schweitzer are in direct contradiction with the statements of H. Rose.

A number of experiments showed that neither an excess

of solution of ammonium carbonate, nor a prolongation of the time of action, nor an alteration of the degree of concentration, led to satisfactory results. All the experiments confirmed the view of Schweitzer that barium and strontium sulphates, when mixed, behave quite differently from what would be assumed from the behaviour of the separate sulphates with ammonium carbonate. If barium sulphate predominates strontium sulphate escapes decomposition, and if strontium sulphate exists in excess barium sulphate is converted into carbonate. Both reactions occur more or less simultaneously, and sometimes the errors arising may happen to compensate each other.

Experiments were also made on the application of a mixture of potassium carbonate and sulphate. Here also satisfactory results could not be obtained by any modification of the process. Thus a trustworthy separation of barium and strontium cannot be effected in this manner.

—*Zeitschrift für Analytische Chemie.*

NOTE ON THE PURIFICATION OF ALCOHOL FOR LABORATORY USES.

By E. WALLER, Ph.D.

COMPARATIVELY recently several papers have appeared on the subject of the reactions of potassium permanganate with alcohols, and the impurities which they may contain.*

In preparing alcoholic solutions of caustic alkalies, and also of silver nitrate (for fat tests, &c.), I have been annoyed, as have other chemists, by the unsatisfactory character of the solutions obtained in consequence of the presence of impurities in the alcohol bought for laboratory use. I find also that most alcohol of 93 per cent, when kept in tin cans, slowly reacts on the tin, giving, after a while, a cloud of SnO_2 , which is too fine to filter out, and renders purification by distillation necessary. In the light of the results obtained by the writers above alluded to, I have adopted the following method for the purification of my alcohol, on which I ask the criticism of the members of the Society:—

A convenient amount of the alcohol to be purified is shaken with pulverised potassium permanganate until it assumes a decided colour. It is then allowed to stand for some hours, until the permanganate has been decomposed and brown manganese oxide is deposited. A pinch of pulverised calcium carbonate is then added, and the alcohol distilled at the rate of about 50 c.c. in twenty minutes from a flask provided with a Wurz tube or one of the Lebel-Heninger pattern. The distillate is tested frequently until about 10 c.c. thereof, when boiled with 1 c.c. of strong (syrupy) solution of caustic soda or potash, gives no perceptible yellow colouration on standing for twenty minutes or half an hour. What distils over after that time is preserved for use.

The first distillates may be added to the small amount remaining in the distilling flask (which should not be driven down to complete dryness), and a fresh portion of purified alcohol recovered.

The rationale of the proceeding appears to be that the permanganate oxidises and destroys chiefly the fusel oil, furfural, and other compounds of that nature, the acids resulting from the reaction are neutralised by the calcium carbonate added before distillation, and by distilling slowly the aldehyd, at least, is concentrated in the first portions of the distillate. Distillation of alcohol containing caustic potash or soda seemed to cause a constant formation of aldehyd. The alcohol thus purified is perfectly neutral, and gives most satisfactory results when

* Habermann, *Pres. Ztschr. Anal. Chem.*, xxvii., 663. Rose, *ib.*, xxviii., 355. Cazeneuve, *Bull. Soc. Chim.* (Paris), [3] i., 700. See also *Dingl. Polyt. Jour.*, cclxxiii., 374.

used as a solvent for caustic alkalies or silver nitrate, the solutions remaining as colourless as distilled water, even after boiling and standing indefinitely, if properly protected from dust and other external influences.—*Journ. Am. Chem. Soc.*

THE TECHNICAL ANALYSIS OF WOLFRAMITE.

By B. SETLIK.

THE author pulverises the mineral finely and dries it at 110°. For the analysis from 3 to 5 grms. of the sample are melted for about two hours in a platinum crucible with from three to four times the weight of sodium carbonate. The melted mass along with the crucible is then boiled in water until nothing remains adhering to the sides. The crucible is then rinsed with water, the solution is filtered, and the residue is washed until the waters are no longer rendered turbid by hydrochloric acid. The alkaline solution, while hot, is poured into an excess of hydrochloric acid, and the whole is then boiled for half an hour in order that the precipitate may be the more readily decanted. This deposit, consisting chiefly of tungstic acid (along with which there may occur stannic, silicic, and molybdic acids), is washed, dried, ignited, and weighed. When igniting the precipitate must first be removed and incinerated with ammonium nitrate.

The ignited residue is treated with 4 c.c. hydrofluoric acid in an air-bath, evaporated to dryness, and again ignited. This removes the silica, which is almost always present. If the wolframite contains no tin, the weight of the precipitate, when freed from silica, shows the proportion of WO_3 . If tin is present it is best determined as follows, calculated as SnO_2 , and deducted from the weight of the mixture $WO_3 + SnO_2$.

The mixture of the two acids is fused for half an hour with potassium cyanide, the melt is dissolved in water, the residue of metallic tin is filtered off, dissolved in ferric sulphate, and titrated with permanganate. If the manganese and iron are to be determined, the residue of the soda melt is dissolved in hydrochloric acid and the solution is divided into two equal parts; the one is reduced with zinc and titrated with permanganate to give the quantity of iron, and the other part is precipitated with sodium carbonate and oxidised with chloride of lime. The precipitate is decanted, filtered, washed, and, together with the filtrate, dissolved in ferrous sulphate of known strength, when the excess of ferrous sulphate is titrated back.

The tungstic acid in wolframite generally ranges between 60 and 80 per cent, and that of manganese between 10 and 20. The tungstic acid in scheelite may be determined in the same manner.—*Chemiker Zeitung*.

THE ESTIMATION OF MINUTE QUANTITIES OF GOLD.*

By Dr. GEORGE TATE, F.I.C., F.C.S.,
Principal at the College of Chemistry, Liverpool.

(Continued from p. 46).

The Parting and Fusion of the Gold into a Bead.—In the estimation of minute quantities of gold, with which this paper only deals, remove the silver-gold alloy from the cupel and place it in a small clean porcelain crucible; add one, two, or more drops of pure nitric acid (diluted with half its bulk of distilled water), according to the amount of alloy, and gently heat upon wire gauze by means of a small flame until all action appears to have

ceased. The Bunsen burner or spirit lamp should be held in the hand, so that when violent ebullition commences the heat may be quickly withdrawn.

When the silver is in appreciable excess of the gold ($2\frac{1}{2}$ to 1) the former metal dissolves, leaving the gold as one black spongy mass, or as a number of particles. In the latter case the particles may be made to cohere by slightly turning the crucible between the fingers and causing them to touch. About half fill the crucible with distilled water, allow the gold particles to settle, and then decant off the fluid by pouring against the finger used as a decanting rod. The contents of the crucible should be carefully watched during this decantation, so that no gold particles are allowed to escape. Fresh water is then added, and the liquid again decanted. If the silver has been appreciable in amount, the washing may be repeated a second or third time.

The crucible, and with it the gold, is dried on an iron plate or wire gauze, kept warm by a small flame. If a strong heat is applied the metal diminishes in bulk, acquiring the yellow colour of gold, and cannot then be so readily removed. Cut a small piece of lead (as free as possible from silver, and weighing about half a grain) with a smooth flat surface. Hold the lead upon the point of a penknife, and press the bright surface upon the particles of gold; the latter generally firmly adheres to the lead. Transfer the lead, and with it the gold, carefully to a small bone-ash cupel. The gold will then be on the under surface of the metal and protected from loss during the next operation of cupellation.

This cupellation is performed in the manner described for the preparation of standard prills, or by placing the cupel containing the metal in the muffle of an ordinary muffle furnace, or in a miniature furnace that may be constructed for the purpose. The prill of gold left after cupellation should have a bright golden colour and rounded form. If not round it can be again picked up on a piece of lead, and again cupellated. The measurement and estimation of the weight of the prill is performed in the way previously described.

The cupels that are employed by myself are made from very fine prepared bone-ash, and are about $\frac{1}{4}$ in. in height and $\frac{3}{8}$ in. wide. The mould was fashioned from an old file handle from which the brass ring or ferrule of the above dimensions was removed; on to the round end of the wooden handle was fixed a round-headed brass nail such as are used for ornamental purposes; the end of the handle from which the ring had been removed was slightly lessened in size so that it readily slipped into the ring. To prepare a cupel, stiffen the bone-ash with water, press some into the ring-mould, fashion a cup-shaped depression with the rounded end of the handle, and then force out the moulded ash with the other end. Keep the cupels for some time in a warm place, and then heat them for a few minutes in the muffle-furnace. If the bone-ash has been originally fine, such cupels are fairly strong, freely absorb fused litharge, and are even, when viewed under the microscope, smooth in texture and much superior (for cupellations in miniature) to the ordinary cupels employed for assaying, since among the irregularities of these latter, minute gold prills are very often lost. Moulds of various sizes can be made in the above way; the moulds also serve for making miniature clay scorifiers, and by a little alteration of the moulding rod, for clay crucibles suitable for miniature assays.

A miniature muffle-furnace may be constructed out of two plumbago crucibles, 4 to 5 inches high, to serve as the furnace body, and a short length of porcelain or fire-clay tube of 1 to $1\frac{1}{2}$ inch bore to serve as a muffle. By means of a penknife, cut the bottoms from the two crucibles. One crucible is supported mouth upwards in the ring of a retort stand, and upon the mouth (in semi-circular depressions that have been cut with a knife) is placed the porcelain or clay tube; the tube is then covered with the other crucible, cut in the lip in the same manner as the under one. The furnace as thus constructed

* A Paper read before the Liverpool Polytechnic Society, November 1889.

is open at the top and bottom, and tapers down and up from the muffle. The muffle is heated by a Fletcher or other convenient blowpipe from the lower orifice, and with a good blast can be brought to the temperature necessary for cupellation in two or three minutes. Doors for the two ends of the tube may be constructed out of the crucible bottoms. In place of the tube, a small sized triangular crucible, in the bottom of which a hole is drilled, will serve as a muffle.

When the gold obtained by parting appears to be less than the thousandth of a grain, it is generally advisable to cupellate with lead (so as to obtain the prill) in a muffle, rather than by the blowpipe, since the cupel is then less liable to crack and no risk is incurred of loss of the gold by its being mechanically carried away by the force of the blast from the blowpipe.

Utility and Accuracy of the Measurement Method.—The following considerations will point out the utility of the application of the microscope to the assaying of gold ores and auriferous metal.

An ore yielding an assay 6 dwts. 12 grains of gold per ton (or 0.001 per cent) is generally an ore that pays for working, yielding a slight margin of profit. Where the assay balance is employed for weighing the gold obtained by assay, at least 500 grains (or 32 grms.) would be required to be assayed so as to estimate the proportion of metal per ton within an error of 1 dwt. Such an ore in this quantity would yield on assay 5 one-thousandths of a grain. The gold from the same, or even one-half of the above quantity of ore, could be estimated with one half of the above possible error by means of the microscope. Upon 10 grains, if they could be trusted as being a representative sample of the rock, yielding an unweighable quantity of gold, a prospector could quickly estimate the proportion of gold within an error of 1 dwt. per ton. In other words, a skilful manipulator of the blowpipe, with the aid of a microscope, could, with comparatively few and simple apparatus, quickly perform rough assays of rock or trace the yield of gold in different parts of a bearing lode, or, by comparative tests, obtain valuable indications of the genuineness, or, otherwise, of auriferous rock when taken from the mine.

By working upon 1000 grains of rock or metal (65 grms.), gold in the proportion of only 2 grains per ton has been obtained and estimated by this method of measurement—the estimate erring presumably only to the extent of 20 per cent; since, the author has found that the one ten-thousandth of a grain (0.0005 m.grm.) can be parted even from many thousand times its own weight of silver with a loss of gold less than the percentage above mentioned, and that even the millionth of a grain of the metal still leaves some proportion after parting from silver and collection by lead.

Needless to say, the litharge employed for the assay by fusion should itself be free from any such proportion of gold as might entirely nullify the accuracy of the assay conducted with its aid. A method for the purification of litharge has been previously described.

The commercial litharge employed for my experiments yielded (by assay of 2 lbs.) gold in the proportion of only one-hundredth of a grain per ton.

No doubt the most scientific worker is apt at times to overrate the powers of any method of analysis or estimation that has been found by him to give accurate results.

It is impossible to free the mind from some trace at least of prejudice. I am glad, therefore, to be able to give more or less independent evidence of the extreme degree of accuracy to which gold estimations may be carried by means of the microscope. This opportunity has been afforded me by a sceptical friend—Mr. A. H. Knight—who has had considerable experience in gold assaying, but who, I think, will in future, in necessary cases, weigh his gold with the microscope.

Mr. Knight introduced, by means of an alloy of lead, gold, and silver, known quantities of gold into assay lead,

and supplied me with six portions of alloy, in each of which he required me to estimate the total gold.

In each case I cupelled and parted the gold from the silver, collected and weighed by measurement in the manner described. The following are my returns, side by side with the calculated quantities of gold assumed to be present, on the assumption that Mr. Knight's alloy of gold was uniform throughout* :—

Sample No.	Estimated weight of gold (U.T.). Grain.	Actual quantity of gold (A.H.K.). Grain.	Error in weight.	Error in per cent.
1	0.0052	0.00499	+0.00021	+4
2	0.0100	0.00991	+0.00009	+1
3	0.0026	0.00242	+0.00018	+7
4	0.0012	0.00132	-0.00012	-8
5	0.00066	0.000678	-0.000018	-3
6	0.00028	0.000244	+0.000036	+14

In actual weight, the greatest error is approximately two one-ten-thousandths of a grain of gold (or 0.013 m.g.), the smallest error is approximately two one-hundred-thousandths of a grain (0.0013 m.g.).

(To be continued).

NOTE ON THE MOLECULAR VOLUMES OF AROMATIC COMPOUNDS.

By JŌJI SAKURAI, F.C.S.
Professor of Chemistry, Imperial University.

It is well known that the observed molecular volumes of benzene and its derivatives are less than those calculated with the use of Kopp's constants, which, when applied to saturated fatty compounds, give results fairly agreeing with the observed values.

Other values for carbon and hydrogen to be applied to benzene (and its derivatives?) have therefore been calculated. Lotter Meyer regards the hydrogen of benzene as having the value 5.† instead of 5.5, while the carbon is regarded as having the value 11, as in saturated fatty compounds. Löschmidt assumes that half the carbon atoms in benzene have the value 11, and the remainder the value 14, and that hydrogen has the constant value 3.5.

Each of these sets of values, I consider, has been arbitrarily deduced from the observed specific volume of benzene, and therefore, when calculated back, they naturally give results agreeing with the latter.

Meyer's calculation.	Löschmidt's calculation.	Observed.
$C_6 = 6 \times 11 = 66$	$C_3 = 3 \times 14 = 42$	
$H_6 = 6 \times 5 = 30$	$C_3 = 3 \times 11 = 33$	
	$H_6 = 6 \times 3.5 = 21$	
	96	95.9

Now, Meyer's and Löschmidt's constants are only applicable to benzene, and cannot be regarded as giving results agreeing with the observed values when applied to the homologues of benzene. For,—

1. If we regard these constants to be applied to the side chains as well, then the calculated values of the homologues of benzene would be less than the observed values; for, while benzene possesses abnormally low molecular volume, its homologues show the constant increase of 22 in the volume for an increment of CH_2 . The hydrogen in the side-chain cannot, therefore, possess the value 5, and still less the value 3.5.

* I have convinced myself that gold-lead alloys containing minute quantities of gold are practically uniform in composition.

† I have not been able to refer to Meyer's original paper. Thorpe (*Journ. Chem. Soc. Trans.*, 1880, 381) states—"Lotter Meyer makes $H=3$," . . . but this I regard as a misprint for $H=5$. This misprint is reproduced in "Watts's Dict.," III. Suppl., p. 2256, and again in Mr. Kuhara's paper to be referred to later on.

	Observed.		Calculated.
	Kopp.	Schiff.	C=14 and H=3.5.
Benzene, C_6H_6	95.8	95.94	96
Toluene, $C_6H_5.CH_3$	—	117.97	114
Xylene, $C_6H_4.(CH_3)_2$	—	139.74	132
Ethyl benzene, $C_6H_5.C_2H_5$	—	138.93	132
N. propyl benzene, $C_6H_5.C_3H_7^a$	—	161.82	150
P. Ethyl toluene, $C_6H_4.CH_3.C_2H_5$	—	161.94	150
Mesitylene, $C_6H_3.(CH_3)_3$	—	162.41	150
Cymene, $C_6H_4.CH_3.C_3H_7^a$	183.5	184.46	168
Naphthalene, $C_{10}H_8$	149.2	—	147 or 153†

2. If we regard the above constants as applicable to the benzene nucleus only, and the carbon and hydrogen in the side-chain as possessing their normal values, then the use of Meyer's constants means an advantage of 2.5 units over Kopp's values for one atom of hydrogen replaced by CH_3 , C_2H_5 , &c.; for $C_6H_5=91$ instead of 93.5. For di-substitution products the advantage is 2.0, for tri-substitution products 1.5, and so on, until we shall find in hexamethyl-benzene, for example, a body possessing normal molecular volume. This, however, does not seem to be the case. The use of Löschmidt's constants for only the benzene nucleus leads to a singular result. For mono-substitution products the advantage over Kopp's constants is 1 unit, as $C_6H_5=92.5$ instead of 93.5; but for di-substitution products the disadvantage is 1 unit, for tri-substitution products the disadvantage is 2 units, and so on.

Meyer's and Löschmidt's constants are, therefore, only applicable to benzene, and not to its homologues with any strictness.

I have calculated another value for carbon which, I admit, is as arbitrary as Meyer's or Löschmidt's, but which has the merit of being applicable to aromatic hydrocarbons in general. I regard each of the six atoms of carbon in benzene nucleus as having the value 10.5, while the hydrogen of the nucleus, as well as the carbon and hydrogen of the side-chains, possess their normal values, viz., C=11 and H=5.5.

This consideration is, of course, derived from the observation that the replacement of hydrogen in benzene by CH_3 , C_2H_5 , &c., causes the same increase in volume as in saturated fatty compounds.

The following comparison will make the above statement clear, the numbers under "observed" being those obtained by R. Schiff.* Kopp's determinations of benzene, cymene, and naphthalene are also added. The ten atoms of carbon, in the last hydrocarbon, constituting the two benzene nuclei are each of them regarded as having the value 10.5.

	Observed.	Calculated.
	Kopp.	Schiff. C=10.5 & H=5.5.
Benzene, C_6H_6	95.8	95.94 96
Toluene, $C_6H_5.CH_3$	—	117.97 118
Xylene, $C_6H_4.(CH_3)_2$	—	139.74 140
Ethyl benzene, $C_6H_5.C_2H_5$	—	138.93 140
N. propyl benzene, $C_6H_5.C_3H_7^a$	—	161.82 162
P. ethyl toluene, $C_6H_4.CH_3.C_2H_5$	—	161.94 162
Mesitylene, $C_6H_3.(CH_3)_3$	—	162.41 162
Cymene, $C_6H_4.CH_3.C_3H_7^a$	183.5	184.46 184
Naphthalene, $C_{10}H_8$	149.2	— 149

The value 10.5 for nucleus carbon thus adapts itself well either for benzene or its homologues; and in the deducing of such special values for carbon or hydrogen, or for both, the aromatic hydrocarbons are certainly the most suitable, as they consist of carbon and hydrogen alone, and do not contain oxygen or nitrogen, the presence of which introduces elements of uncertainty.

The above value of carbon may, however, be employed in the same manner in calculating the molecular volumes of simpler aromatic compounds containing oxygen,

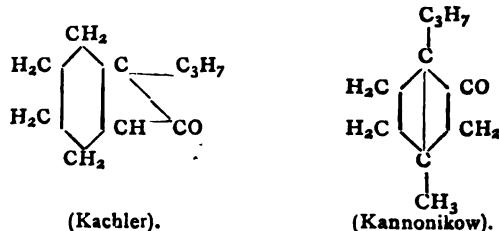
the two values given to this element by Kopp being adopted in the calculation. Thus—

	Observed.	Calculated.
	(Kopp).	C=10.5 & H=5.5. O=12.2 & 7.8.
Phenol, $C_6H_5.OH$	103.6	103.8
Benzoic aldehyd, $C_6H_5.CHO$	118.4	119.2
Benzoic acid, $C_6H_5.CO.OH$	126.9	127.0
Ethyl benzoate, $C_6H_5.CO.O.C_2H_5$	172.4—174.8	171.0
Benzyl alcohol, $C_6H_5.CH_2.OH$	123.7	125.8

Mr. Kuhara* calculated the molecular volumes for the above bodies, using Löschmidt's constants, and on the supposition that 3 atoms of carbon have the value 14, the rest 11, and that hydrogen, whether of the nucleus or of the side-chain, possesses the constant value 3.5. He will find that his numbers are not more concordant with the experimental values than are those above calculated. If, moreover, he tried his method of calculation upon the aromatic hydrocarbons,—bodies which, as I already pointed out, are certainly best suited to test the accuracy or utility of the constants for carbon and hydrogen—he will get very different results, as I have already broadly indicated and as the above Table will show in greater detail.

The above Table clearly shows the fault of the method of calculation employed by Mr. Kuhara, which, when applied to simpler aromatic compounds containing oxygen, gives results (by chance?) fairly agreeing with the experimental values, but which when applied to the aromatic hydrocarbons gives results entirely at variance with those experimentally determined.

Using the same method of calculation, and on the supposition that oxygen is ketonic, Mr. Kuhara finds that the observed molecular volume of camphor agrees almost exactly with the calculated value, and draws therefore a probable conclusion that its constitution is correctly represented by one of the following formulæ:—



The agreement between the observed and the calculated values for the molecular volume of camphor, viz., 187.42

* Jour. Science College, Imp. Univ., Japan, vol. ii., Part 4; also Jour. Tokyo Chem. Soc., vol. ix., No. 9, and CHEMICAL NEWS, vol. ix., p. 14.

† Mr. Kuhara makes naphthalene = 150, but it seems to me that the two possible ways of calculation consistent with those adopted for other bodies are:—

I.		II.	
$C_6 = 3 \times 14 = 42$		$C_6 = 5 \times 14 = 70$	
$C_7 = 7 \times 11 = 77$		$C_7 = 5 \times 11 = 55$	
$H_8 = 8 \times 3.5 = 28$		$H_8 = 8 \times 3.5 = 28$	
	147		153

and 18.72 respectively, is certainly very remarkable, but one does not feel very much inclined to accept any conclusion based upon a method of calculation apparently open to so grave a criticism as I have indicated.

With our present imperfect state of knowledge regarding the relation between molecular volumes of compounds and their "constitution," especially in the case of aromatic compounds, we can neither make a free nor a safe application of it in the discussion of the probable constitution of such bodies as camphor and borneol.

It is probable, for instance, that the atomic volume of carbon may vary not only according as it exists in the benzene nucleus or in the side-chains, but also according as it is combined with 1, 2, 3, or 4 other carbon atoms, and again according to the nature of other atoms directly combined with it. Schiff, indeed, has pointed out that the atomic volume of carbon may vary from 8 to 13, and that of oxygen from 5.6 to 19.

The difference observed between the molecular volumes of—

- (1) Para-chlorotoluene .. $C_6H_4.CH_3.Cl = 134.91$
(2) Benzylic chloride.. .. $C_6H_5.CH_2.Cl = 133.47$

may, for example, be due to either one or all of the following differences:—

1. Chlorine in (1) is in direct combination with carbon of the nucleus, that in (2) with one in the side-chain.
2. There are four (CH) groups in (1), five in (2); in other words, there are two side-chains in (1), and only one in (2).
3. The carbon to which chlorine is combined in (1) is in its turn directly combined with two other atoms of carbon, while that to which chlorine is combined in (2) is only combined with one other carbon atom.

Such considerations as these make us hesitate very much before making a free application of the very imperfect knowledge we possess at present regarding the relation between molecular volume data and the constitution of chemical compounds.

It is true that the molecular volume of camphor calculated with the use of constants, $C=10.5$ and $H=5.5$, $O=12.2$ or 7.8 , does not agree with the experimental value, but this is simply because we are ignorant of the law which connects together the variation of the atomic volume of an element with its mode of combination. It is possible, for example, that the atomic volume of carbon directly combined with four other atoms of carbon may be considerably lower than 10.5 or 11 ,* and the abnormally low molecular volume of camphor, as actually observed, may be due to the existence in it of two or more of such carbon atoms. The six formulæ of camphor quoted by Mr. Kuhara represent it as containing respectively 0, 0, 2, 1, 2, and 1 such carbon atoms, and it may possibly turn out that either the formula (3) or the formula (5) correctly represents its constitution. Further theoretical speculations upon these points are more than useless at present, and I therefore do not more than briefly make the above suggestions for future consideration.

On the Dioxystearic Acid obtained by the Oxidation of Oleic Acid in an Alkaline Solution by Means of Permanganate.—Nik. Spiridonoff.—In this process there are chiefly formed caprylic, suberic, and azelaic acids. These substances, which are formed during the production of dioxystearic acid, must be in part regarded as products of a further oxidation of the latter acid.—*Journal für Praktische Chemie*, Vol. xl., No. 16.

* It may be remarked that the atomic volume of diamond calculated in the usual manner is $\frac{12}{3.53} = 3.4$.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1889.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MESSRS. Wallace C. Nickels and J. A. Nettleton were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Frederick Alfred Anderson, B.Sc., Lesney House, Erith, Kent; G. Russell Beardmore, Warwick House, Upper Street, Islington; Robert Frederick Blake, 37, Hartington Street, Dublin Road, Belfast; Bertram Blount, Laboratory, Broadway, Westminster; Henry Herbert Bunting, 82, Netherwood Road, Kensington, W.; Paul Alexander Cobbold, Warwick School, Warwick; John S. Lumsden, 5, Paradise Road, Dundee; Frederick Mills, Bevan Crescent, Stockton-on-Tees; Robert Richard Rothwell, 82, Mawson Street, Ardwick Green, Manchester; Edward Sergeant, 75, Park Road, Bolton; Basil William Valentin, Aston Brewery, Birmingham.

The following papers were read:—

1. "A New Method of Estimating the Oxygen Dissolved in Water." By J. C. THOMAS, D.Sc., M.B.

The process is based on the observation that whereas, in absence of oxygen, nitrous acid and hydrogen iodide interact to form iodine, water, and nitric oxide; in presence of oxygen the nitric oxide becomes re-oxidised, and, serving as a carrier of the oxygen, an amount of iodine equivalent to the oxygen present is liberated, in addition to that resulting from the initial action of the nitrous acid: hence, deducting the amount liberated by the nitrous acid and by the oxygen dissolved in the solutions used from the total amount, the difference will be that corresponding to the oxygen dissolved in the water examined.

The solutions used are:—(1) A solution containing 0.5 gm. sodium nitrite and 20 grms. potassium iodide in 100 c.c.; (2) a solution of 7.75 grms. sodium thiosulphate in 1 litre, 1 c.c. of which corresponds to 0.25 milligram of oxygen; (3) a clear solution of starch; and (4) diluted pure sulphuric acid (1:3).

The apparatus required is a very simple one. It consists of a wide-mouth white glass bottle of about 500 c.c. capacity, provided with a caoutchouc stopper, through which four holes are bored. Through one passes the neck of a cylindrical "separator" funnel of known capacity, and through the second a tube drawn out to a fine point, which is connected by a short length of caoutchouc tubing with the thiosulphate burette; while inlet and exit tubes for coal-gas are passed through the third and fourth holes, the exit tube having attached to it a sufficient length of caoutchouc tubing to permit of connection being established between the bottle and the separator when the stopper of the latter is withdrawn.

The separator is filled with the water to be examined, and 1 c.c. of the nitrite-iodide and 1 c.c. of the acid solution are added; if the pipette be held vertically, with its end just below the surface of the water, the solutions flow in a sharply defined column to the lower part of the separator, so that an infinitesimally small quantity (if any) is lost in the water which overflows when the stopper is inserted. The admixture of the liquids having been effected by inverting the apparatus several times, a sharp current of coal-gas is passed into the bottle to displace the air, the escaping gas being allowed to burn at a jet attached to the exit tube. Fifteen minutes after adding the solutions to the water the flame is extinguished, a cork is attached in place of the jet and is inserted in place of the stopper of the separator, and the water is then allowed to flow into the bottle; the exit tube having been disconnected from the funnel and the gas set fire to, thio-

TABLE I.
COMPOSITION OF THE MILK.

Yield of milk.		Date.	No. 40.			No. 41.		
40	41		Morning.			Evening.		
38 lbs.	37 lbs.		Fat.	Other solids.	Total solids.	Fat.	Other solids.	Total solids.
—	—	13th Nov.	3.41	8.47	11.88	5.71	8.63	14.34
—	—	19th "	—	—	—	—	—	—
—	—	22nd "	3.39	8.39	11.78	4.50	8.38	12.88
22 "	25 "	5th Dec.	3.44	8.28	11.72	5.12	8.48	13.60
—	—	10th "	2.17	7.87	10.04	4.68	8.30	12.98
15 "	22 "	17th "	2.98	7.58	10.56	3.86	8.14	12.00
8 "	18 "	7th Jan.	2.70	7.50	10.20	3.64	7.68	11.32
			3.93	8.13	12.06	4.95	8.19	13.14

TABLE II.

SO_3	$\text{As}_2\text{O}_3, 8\text{SO}_3$	$\text{Sb}_2\text{O}_3, 9\text{SO}_3$
$2\text{H}_2\text{SO}_4, \text{SO}_3$	$\text{As}_2\text{O}_3, 4\text{SO}_3$	$\text{Sb}_2\text{O}_3, 4\text{SO}_3$
H_2SO_4	$\text{As}_2\text{O}_3, 2\text{SO}_3$	$\text{Sb}_2\text{O}_3, 3\text{SO}_3$
$9\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ to $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$	$\text{As}_2\text{O}_3, \text{SO}_3$	or $\text{Sb}_2(\text{SO}_4)_3$
$\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$
$\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$	—	or $\text{Sb}(\text{OH})\text{SO}_4$
Action on sulphate of alcohol	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3$
Cold water	As_2O_3	or $\text{SbO}(\text{SO}_4)_2$
Hot water	—	$2\text{Sb}_2\text{O}_3, \text{SO}_3, x\text{aq.}$
		$7\text{Sb}_2\text{O}_3, 2\text{SO}_3, y\text{aq.}$

Where, $x=4$ to 16 and $y=2$ to 16.

sulphate is run in until the colour of the iodine is nearly destroyed; about 1 c.c. of starch is then added from the separator and the titration is completed. The effect of the nitrite, dilute acid, and starch solutions is readily determined by removing the separator and adding 5 c.c. of each in succession and then titrating; the effect of the oxygen in the thiosulphate may be allowed for on the assumption that as much oxygen is dissolved in it as distilled water would contain at the same temperature. It appears that there is no advantage in passing the coal-gas through alkaline pyrogallol.

The author states that concordant results are easily obtained, and that the results in the case of freshly distilled water closely agree with those recently published by Sir Henry Roscoe and Mr. Lunt (*cf. Chem. Soc. Proc.*, 1889, 124; *Trans.*, 1889, 552). Thus:—

Temp.	Thresh.	Roscoe and Lunt.
10°	7.81	7.77
15	7.02	6.96
20	6.17	6.22
25	5.69	5.60
30	5.45	5.43

DISCUSSION.

Mr. WARINGTON said that on the occasion of Mr. Holland having suggested in the *CHEMICAL NEWS* a method of estimating nitrites in water by means of potassium iodide, he had pointed out that the method was fallacious in presence of air; the delicacy of the iodine test for nitrites was doubtless ascribable to the occurrence of the series of changes of which Dr. Thresh had availed himself.

Mr. GREEN stated that he also had called attention to the influence of oxygen about four years ago, in a communication to the University College Chemical Society.

Dr. STEVENSON said that he was not satisfied with the method of estimating nitrites in water proposed by the author; a comparison with other methods would be desirable.

Mr. CHAPMAN JONES drew attention to the use of manganous hydrate in estimating the oxygen dissolved in water.

2. "Note on a Milk of Abnormal Quality." By F. J. LLOYD.

The author is led to give the results of his examination of the milk afforded by two cross-bred shorthorns, as its quality appears to be altogether remarkable (compare table); there being no evidence either that the cows were suffering from disease, or that they were insufficiently or improperly fed, he is of opinion that the normal quality of their milk is such as has never been recorded. Several complete analyses, made with the object of discovering whether the loss fell on any special constituent, show that this is not the case, the caseine, sugar, and other constituents, except the mineral matters, being equally affected (See Table I.).

DISCUSSION.

Dr. STEVENSON expressed the opinion that the animals in question were in some way suffering from malnutrition, or were subject to some latent disease.

Mr. WARINGTON said that the amount of total solids was not below the accepted lowest value; whilst Professor KINCH remarked that equally low results had been obtained in certain cases at the Agricultural College, Cirencester.

Professor THOMSON mentioned the case of a cow having the propensity of eating heather tops affording a milk containing a lower proportion of total solids than that of other cows of the herd which had not the propensity.

Mr. LLOYD, in reply, said that in the cases considered by him the small amount of solids other than fat was what he desired to bring under notice; the total solids often varied, but the variation was chiefly in the amount of fat, not in the solids other than fat.

3. "The Sulphates of Antimony." By R. H. ADIE, B.A.

Having previously studied the compounds of arsenious oxide with SO_3 , the author has now examined those of antimonious oxide. His results are summarised in the following Table, in which is indicated the composition of the products obtained from the two oxides on treatment with the acid formulated in the first column (See Table II.).

On comparing the two series of compounds it appears that:—

(i.) With H_2SO_4 and weaker acids, Sb_2O_3 forms a different order of sulphates from As_2O_3 , while it resembles it in forming acid sulphates when subjected to the action of stronger acids. Thus the former yields the characteristic group salt, $Sb_2(SO_4)_3$, in place of the basic $As_2O(SO_4)_2$ afforded in the latter. The limits of existence, both as regards dilution and temperature, are much narrower for the arsenic than for the antimony salt. The practically complete formation of $Sb_2(SO_4)_3$ in one crystallisation also contrasts with the formation of $As_2O(SO_4)_2$ only by repeated crystallisation.

(ii.) Arsenious oxide does not form any basic sulphates containing water, while the more metallic antimonious oxide does form hydrated sulphates in acids weaker than $H_2SO_4 \cdot H_2O$. This acid is the limit of existence of $Sb_2(SO_4)_3$ in solution, and of any arsenic sulphate whatever.

At the meeting on March 20th, Professor Judd, F.R.S., will deliver a lecture on "*The Evidence afforded by Petrographical Research of the occurrence of Chemical Change under great Pressures.*"

At the next meeting, on February 6th, there will be a ballot for the election of Fellows, and the following papers will be read:—

"The Oxides of Nitrogen." By Professor RAMSAY, F.R.S.

"Studies on the Constitution of Tri-derivatives of Naphthalene." By Dr. ARMSTRONG and W. P. WYNNNE.

NOTICES OF BOOKS.

Annual Report of the Public Analyst appointed for the Parish of Kensington for the Year ending March 31, 1889. By C. E. CASSAL, F.C.S., F.I.C. Kensington: J. W. Wakeham.

In this parish the adulteration of milk seems to be progressively declining. In the year 1885—86 the genuine samples were 29.0 per cent; in 1886—87, 37.86; in 1887—88, 55.46; and in 1888—89, 58.33 per cent. The proportion of samples inferior in quality, though not positively adulterated, shows no such progressive decline.

Two of the samples of butter pronounced adulterated contained, respectively, not less than 93 and 90 per cent of foreign fat. From the returns of the Local Government Board it would appear that the sophistication of butter and the sale of butter substitutes as butter are still very extensively practised.

None of the samples of cheese examined were adulterated.

Two samples of tea, certified as inferior, though not demonstrably adulterated, probably contained a proportion of leaves which had been previously exhausted and re-dried. This fraud is difficult to detect analytically. It is to be feared that the servants in hospitals, boarding-schools, hotels, restaurants, &c., dispose of spent tea-leaves to itinerant agents for this purpose.

A sample of lard was found to have been adulterated with cotton-seed oil and another contained portions of light animal membranes distributed through it.

Several cases which have been made the subject of legal proceedings have given room for great dissatisfaction on the decisions of the Bench. In one case of milk the analyst had certified the presence of at least 25 per cent of water, and the public analyst of another parish had arrived at the same result. The defendant, however, applied to have a sample forwarded to Somerset House for analysis. The chemists there certified that not less than 22 per cent of water had been added. The slight discrepancy would doubtless be due to the time that had elapsed before the second analysis could be made. The Bench convicted the defendant, but although

he had given all this trouble, and though he had been previously cautioned for selling adulterated milk, they merely inflicted a fine of £1 and costs, for the singular reason that he had been a long time in business!

Another dealer, who was fined £1 10s., had previously been not merely cautioned, but actually convicted.

It seems to us that the provision of the Act that a dealer is to be informed that a sample purchased of him will be analysed, is a grave mistake. The object of inspection is to secure a portion of the article as sold in the common course of business. If the dealer is acting honestly it can make no difference to him, or to the results of the analysis, whether he is thus cautioned or not.

It would produce much good if convictions were duly advertised, at the cost of the defendant, in the local papers.

The Vestry of the Parish of Saint George, Hanover Square. Public Analyst's Report for the Year ended March 25, 1889. June, 1889. London: Wightman and Co.

THIS report is presented by the Public Analyst, C. E. Cassal, F.C.S., F.I.C.

If the repression of fraud in the quality of articles of food and drugs sold goes on but slowly, the fault lies, to a great extent, with the foolish leniency of magistrates. Mr. Cassal states, on the authority of the Local Government Board, that in over 80 per cent of the cases taken into Court, the average fine was only about £1. Hence the offender still finds sophistication profitable, and the public generally, as well as the honest tradesman, are taught to think that frauds of this kind are but a very trifling matter. It appears that the samples of coffee and tea submitted to examination in the Parish of St. George were all genuine, but four samples of cocoa were adulterated with starch in quantities ranging from 20 to 35 per cent, and in addition, with sugar from 25 to 35 per cent. Thus, the genuine cocoa present did not reach 50 per cent. If we consider that starch on the large scale is worth about 1d. per lb., the transaction must be exceedingly profitable to the vendor. Two adulterated samples of butter contained respectively at least 95 and 90 per cent of foreign fats.

In milk there has been an improvement. The percentage of genuine samples has risen from 47.06 per cent in 1887—88 to 66.92 in 1888—89. The adulterated and the inferior have, of course, declined. But Mr. Cassal remarks that the word "genuine" does not imply that the milks so described were all of good quality. Of 93 samples returned as genuine, only 49 were of good quality and 37 were pronounced fair.

The adulterated samples of lard contained at least 25 per cent of foreign fat, chiefly beef-stearine, mixed with cotton-seed oil. Of course, neither of these articles can be objected to *per se*, but they should be sold under their own names.

The Vestry of the Parish of St. Mary, Battersea. The Annual Report of the Public Analyst for the Year ending March 25, 1889. By C. E. CASSAL, F.C.S., F.I.C.

IN this parish butter figures in a discreditable manner. The adulterated samples were 62.5 per cent. Fifteen samples consisted chiefly of margarine, and were seized under the provisions of the Margarine Act of 1887. Considering that provision dealers can sell margarine without interference if they will only label it as such, this state of things shows a preference for dishonesty.

All the samples of cocoa examined were adulterated with starch and sugar to the extent of from 50 to 60 per cent.

No coffee has been condemned. But it is to be regretted that grocers are able to evade the law by selling an article which is most mendaciously styled "Coffee as

in France," or "French Coffee." An opportunity should be taken by Government of stopping up this loophole.

In this Parish the conduct of the magistrate is much to be regretted. In one case, after the Analyst's report had been confirmed by the Somerset House chemists the magistrate declined to convict on the ground that "*the defendant had been put to sufficient expense in the matter.*" "Case B" was proved, but here also the magistrate declined to convict, and adjourned the case *sine die*. Two other cases in which the facts were similar were then withdrawn under protest from the Vestry.

Calvert's Mechanics' Almanack and Workshop Companion for 1890, containing, in addition to the usual Matter of an Almanack, Practical, Technical, and Industrial Information especially instructive to Artizans and Handicraftsmen. London: John Heywood.

We notice here a paper on "Oppositions to Patent Applications," which shows that either patent-law or patent practice is in a very unsatisfactory state. Mr. Lloyd Wise, the author of the paper in question, considers that the practice has been wanting in consistency. But how to remedy the mischief is a difficulty not solved either in the paper before us or elsewhere.

In a paper on "Forms and Sizes of Steel and Iron Plate Test Pieces" we find it stated that a certain size is said to be used by "Mr. Jern Kontoret, Stockholm!" Now "Jern Kontoret" is the name not of a man, but of a Swedish periodical devoted to the interests of the iron trade.

Most of the matter contained in this Almanack does not come within our competence.

CORRESPONDENCE.

SILICA IN ANALYSES.

To the Editor of the Chemical News.

SIR,—Can any of your readers enlighten me as regards the following:—

I have a mineral for analysis which consists of aluminium silicates, iron oxides, hydrates, and silicates, magnesium silicates, together with free quartz sand and mica in an extremely fine state, and a little free hydrated silicic acid, probably the result of decomposition. There is also present about 4—5 per cent of alkali, K_2O and Na_2O , combined probably with the aluminium and silica.

The following is an analysis of the gently ignited material?—

SiO_2	66.24
Al_2O_3	18.36
Fe_2O_3	7.77 and trace of manganese.
MgO	2.65 and trace BaO .
Alkalies, &c. ..	4.98 by difference, and includes also traces of $Cl \cdot SO_3 \cdot P_2O_5$.

100.00

I wish to make the analyses so as to show the SiO_2 in a tabulated form, as follows:—

Sand	
Free hydrated SiO_2	
Combined	

I should be much obliged if anyone would tell me the best method of doing so without resorting to tedious and troublesome processes, as the analyses have to be made rapidly.

I can quite confirm Mr. John Tsawoo-White's (CHEM.

NEWS, vol. lix., p. 244) and Mr. Bertram Blount's (CHEM. NEWS, vol. lix., p. 277) suspicions as to the insolubility of "ignited" precipitated SiO_2 in sodium carbonate solution.—I am, &c.,

High Street, Mitcheldean,
Jan. 21, 1890.

W. J. COOPER.

MADDER LAKES.

To the Editor of the Chemical News.

SIR,—I have lately been examining a considerable number of madder lakes with a view of finding whether they had been touched up with cochineal. I have, however, found it a difficult matter to decide, and therefore write to your journal in the hope of eliciting some information from some of its readers. If the adulteration consisted in the addition of a considerable quantity of cochineal lake, it would, doubtless, be easily detected; but I believe that if there is any adulteration it is not so gross; the colour being merely brightened by the introduction of a little cochineal at the end of the process of manufacture.

I have been experimenting on alizarin lakes lately, and my attention was first directed to the rose madders, &c., by their peculiar tint, tending towards violet when rubbed out thin, and very different from the ruby red that I had become accustomed to in working with alizarin. I therefore bought several little tubes of colour from different firms to examine. I found that if I rubbed out a cochineal lake, ground in oil in a porcelain basin, and then poured strong ammonia over it, the lake immediately turned purple.

I then tried the same test for some of my alizarin lakes, and found them very slightly affected. On now trying the madder lakes of commerce, I found that they nearly all turned purple, and those that did not do so were rather brown than violet in tint.

I next proceeded to examine these lakes through the spectroscope, by shaking them up with a little turpentine and allowing the light to pass through that, or by rubbing them out on a glass plate. I found that the alizarin lake, when strong, absorbed everything, except the red, and on diluting gradually allowed more light to pass through, without any bands, unless a possible dusky in the green, thus differing from an alkaline solution of alizarin itself.

A cochineal lake, on the other hand, allowed the passage of a little violet as well as red, and on dilution three bands in the green appeared; one between the green and yellow, one in the middle of the green, and one, very faint, between the green and blue.

On now examining the suspected lakes, two bands were at once detected, corresponding apparently to the two first bands of the cochineal, and these bands were only found in those lakes which were affected by ammonia. Unfortunately, however, the question was not thus settled, as I found on measuring that these bands were shifted further towards the purple than those of cochineal. Nor has the matter been cleared up by the brightening of an alizarin with cochineal. I find I can easily do so, and the resulting lake is very beautiful, but is not very strongly affected by ammonia, and its bands are in the right place.

Having consequently exhausted my resources, I thought it best to appeal to those of your readers who have special knowledge of this subject, in the hope of being able, in this way, to settle the question.

I should mention, in conclusion, that my lake was prepared from "extreme blue" alizarin, but I also prepared and tested with ammonia lakes from "yellow and "blue" alizarin.

The subject is, I think, of some importance, as, if the ammonia test is reliable, there are hardly any madders

sold for artists' use which have not been touched up with cochineal.—I am, &c.,

King's College, Cambridge,
Jan. 24, 1890.

A. P. LAURIE, M.A.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., No. 10.

Preparation of Nitrogen in the Cold from Atmospheric Air.—M. Berthelot.—The author utilises the reaction of copper in presence of ammonia for the absorption of the oxygen. Nitrogen remains, and is displaced by means of water completely freed from dissolved oxygen by the same reactions. The gas is freed from traces of nitrite and from ammonia by a passage over potassa, or better, soda-lime, first in the liquid and then in the solid state, and afterwards over pumice steeped in sulphuric acid.

Thermic Researches on the Isomeric Nitro-Camphors and on Cyanated Camphor.—MM. Berthelot and P. Petit.

Combination-Heat of Fluorine and Hydrogen.—MM. Berthelot and Moissan.—These two papers do not admit of useful abstraction.

New Researches on the Fixation of Nitrogen by Vegetable Mould. Influence of Electricity.—M. Berthelot.

The Fixation of Atmospheric Nitrogen.—M. Berthelot.

Observations on the Formation of Ammonia and of Volatile Nitrogenous Compounds at the Expense of Vegetable Soil and of Plants.—M. Berthelot.—These three memoirs have already in substance appeared elsewhere.

Facts on Mellitose.—M. Berthelot.—The author has re-examined mellitose as extracted from cotton-seed cakes. He assigns to it the formula $C_{36}H_{32}O_{32} + 5H_2O_2$, but he has also obtained another hydrate containing $6H_2O_2$.

New Observations on the Reciprocal Displacements between Oxygen and the Halogens.—M. Berthelot.—A thermo-chemical paper not admitting of useful abstraction.

Observations on the Presence of Nitrous Acid in the Air.—L. Ilsvay.—The author has found nitrous and nitric acid in the atmosphere at every hour of the day, both acids being in combination with ammonia. He considers that they play an important part in supplying nitrogen to the vegetable economy.

Chemical Treatment of Diseases caused by Cryptogams.—Dr. A. B. Griffiths.—A paper on the use of ferrous sulphate as a remedy for the attacks of parasitic fungi. The subject matter will be found chiefly in the author's papers, "Manures and their Uses," in the CHEM. NEWS and in the *Journal of the Royal Agricultural Society*.

Colorimetric Determination of Nitric Acid by Means of a Sulphuric Solution of Diphenylamine.—J. A. Müller.—This paper will be inserted in full.

Thermic Formation of the Salts of the Phenylendiamines.—Leo Vignon.—This paper does not admit of useful abstraction.

New Apparatus for Fractionated Distillations in a Vacuum.—H. Gautier.—Not intelligible without the accompanying diagram.

Journal für Praktische Chemie.
New Series, Vol. xl., No 16.

Fluorine Compounds of Vanadium and its Nearest Analogues.—E. Petersen.—The result of these researches is that compounds of VOF_2 are formed in neutral or feebly acid solutions. A compound, VF_4 , seems capable of existing in concentrated hydrofluoric acid, but on contact with water or air it is converted into an oxy-fluoride. The compounds in question cannot be directly compared with the known double fluorides of the tetravalent elements, but vanadium approximates more nearly to this stage of oxidation than to any other. The dioxides of niobium and tantalum seem quite indifferent. Among the metals of the iron group, manganese forms a dioxide which possesses feebly acid properties. But it forms, with hydrofluoric acid, sesqui-compounds, and no compounds of tetravalent manganese.

Calorimetric Researches. Nineteenth Memoir: On the Thermic Value of the Acids of the Oxalic Series and of Fumaric and Maleic Acids.—F. Stohmann, Cl. Cleber, and H. Langbein.—The purpose of this investigation was to ascertain how far the numerous isomerism met with in the so-called adipic acids, $C_6H_{10}O_4$, have an influence on their thermic value.

On Opening up Sulphides, such as Bournonite, Proustite, &c., in a Current of Air charged with Bromine.—P. Jannasch.

A New Method for the Analysis of Pyrites.—Paul Jannasch.—These two papers will appear in full.

Remarks on the Determination of Sulphuric Acid in Presence of Iron.—P. Jannasch.—The proportion of sulphuric acid in a liquid, as found by precipitation with barium chloride, is always too low if salts of iron are simultaneously present. The cause of this fact has been recently examined by the author and Richards, on which occasion they discussed the current methods for the analysis of pyrites, and, in reference to that of Lunge, they remarked that from a purely scientific point of view it must be rejected. Thereby they had only Lunge's earlier method in view, which he himself subsequently pronounced not quite accurate. By a previous precipitation of the iron with a slight excess of ammonia at a moderate heat, Lunge has subsequently rendered his process perfectly accurate.

On Opening up Pyrites in a Current of Oxygen.—P. Jannasch.

The Determination of Sulphuric Acid in Presence of Iron.—G. Lunge.—These two papers will be inserted in full.

On Orthoparadinitrophenyl-phenylhydrazine, Dinitro-, and Nitronitroso-azobenzol.—C. Willgerodt and B. Hermann.—Both dinitroso- and nitronitroso-azobenzol dissolve readily in most organic solvents. Hence the molecular magnitudes of these compounds may possibly be determined by means of Raoult's method.

On Orthobromparatoluylic Acid and Chloronitro-Paratoluylic Acid.—M. Fileti and F. Crosa.—A claim of priority as against Claus and Kunath.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 46.

The only chemical matter contained in this issue is a paper by Mr. Riley on the alloys of nickel and steel, taken from *Engineering*, and a note on the sophistication of lard with cotton-seed oil, a fraud which is detected by the iodine test.

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. vii., No. 3.

Recent Methods for Determining the Non-crystalline Matter in the Products of Sugar Works.—G. Midavaine.—In place of Fehling's liquid, Degener and Bodenbinder recommend Soldaini's reagent, which is highly sensitive, and undergoes no change on keeping. To prepare this liquid a solution of 40 grms. pure copper sulphate is precipitated by means of a solution of 40 grms. sodium carbonate, and the precipitate of basic sodium carbonate is filtered and washed. This precipitate, which weighs 15 grms., is gradually introduced into a boiling and concentrated solution of potassium bicarbonate and digested for ten minutes in a vapour-bath. The liquid is then poured into a two-litre flask, made up to a total volume of 1400 c.c., and heated for two hours in a steam-bath, with constant stirring. It is then filtered, and yields a deep blue liquid of the sp. gr. 1.185. If this reagent is boiled, even after dilution, there is no deposit. A solution of pure cane-sugar may be boiled for six minutes over a flame, or for twelve minutes in the brine-bath before the reduction of the reagent takes place. With 50 c.c. of this liquor, 0.0014, or even 0.0005 of inverted sugar may be detected in presence of cane-sugar. Soldaini's reagent keeps almost indefinitely. Another reagent, called the "carbonated liquor," is proposed by H. Pellet, Chief Chemist of the Wanze Sugar Works. It consists of:—Salt of seignette, 200 grms.; sodium carbonate (pure and dry) 100 grms.; copper sulphate (pure and crystalline), 70 grms.; ammonium hydrochlorate, 7 grms.; distilled water, 600 c.c. The four salts are placed in a porcelain capsule, the water is added, and heat is applied until all is dissolved, when the volume is made up to 1 litre, filtering if needful.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Sewage.—Will any reader inform me if sewerage treated with "ferrous sulphate" from a district where the water is chiefly of a greasy character—the sediment when dried and subjected to heat produces a gas giving a good light on combustion—can be of any commercial value.—"STAR."

MEETINGS FOR THE WEEK.

- MONDAY, 3rd.**—Medical, 8.30.
— Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.
— Society of Chemical Industry, 8. "Metallic Compounds of the Phenols," by A. H. Allen. "New Method of Hardening Steel for Projectiles," by Watson Smith. "On Bromanil," by M. Losanich.
— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 4th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
WEDNESDAY, 5th.—Geological, 8.
— Society of Arts, 8. "High-speed Knitting and Weaving without Weft," by Arthur Paget.
THURSDAY, 6th.—Royal, 4.30.
— Royal Institution, 3. "Sculpture in Relation to the Age," by Edwin Roscoe Mullins.
— Royal Society Club, 6.30.
— Chemical, 8. Ballot for the Election of Fellows. "The Oxides of Nitrogen," by Prof. Ramsay, F.R.S. "Studies on the Constitution of the Tri-derivatives of Naphthalene," by Dr. Armstrong and W. P. Wynne. "On the Action of Chromium Oxychlorides on Nitrobenzol," by G. G. Henderson, B.Sc., and J. Morrow Campbell, B.Sc.

- FRIDAY, 7th.**—Geologists' Association, 7.30. (Anniversary).
— Society of Arts, 5. "The Utility of Forests and the Study of Forestry," by Dr. Schlich.
— Royal Institution, 9. "The London Stage in Elizabeth's Reign," by Henry B. Wheatley, F.S.A.
— Physical, 5. (Annual General Meeting). "On Galvanometers," by Prof. W. E. Ayrton, F.R.S., T. Mather, and W. E. Sumpner. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes.

SATURDAY, 8th.—Royal Institution, 3. "The Natural History the Horse, and of its Extinct and Existing Allies," by Prof. Flower, F.R.S., &c.

TO CORRESPONDENTS.

F. MacDonald.—Use a moderately strong solution of nitrate of silver.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1576.

THE COMPOSITION OF THE MILK OF THE BOTTLE-NOSE WHALE (*GLOBIOCEPHALUS MELAS*).

By Prof. PERCY F. FRANKLAND, Ph.D.,
and FRED. J. HAMBLY,
Assistant Lecturer on Chemistry in University College, Dundee.

ON the occasion of the recent capture of no less than 160 individuals of this species in Tankerness Bay, near Kirkwall, Orkney, our colleague, Prof. D'Arcy Thompson, received, amongst other specimens, a small quantity of the milk of one of these creatures, the liquid having been scooped directly from the mammary gland after death.

The sample was unfortunately a very small one (but little in excess of 3 grms.), which is the more to be regretted as an almost unlimited quantity must have been available for collection, a large number of the captured whales being females.

The milk presented a thick creamy appearance, globules of fat being clearly discernible in the mass, which was possessed of a strong fishy odour.

Owing to the small quantity of the material at our disposal, we were unable to make an exhaustive analysis, but such determinations as were possible we deemed it advisable to perform in duplicate, although, from the non-homogeneous nature of the substance, it was not to be anticipated that very concordant results would be obtained.

The following are the results of the duplicate analyses:—

	No. 1.	No. 2.	
Weight of milk taken..	1.431 grms.	1.678 grms.	
<i>Results of Analysis expressed in Parts per 100.</i>			
			Mean.
Total solids (dried at 100— 105° C.)	52.13	50.53	51.33
Water	47.87	49.47	48.67
Non-fatty solids (insoluble in ether)	7.72	7.42	7.57
Fat (soluble in ether)	44.41	43.11	43.76
Ash	0.44	0.47	0.46

That the discrepancies between the two analyses were due to want of homogeneity in the sample, and not to any inaccuracy in the determinations, is clearly shown by the fact that the total solids, non-fatty solids, and fat stand in the same proportion to each other in both analyses. Thus, sample No. 2 was apparently more aqueous than No. 1, and if the results of No. 2 be corrected in the ratio of 50.53 : 52.13, then the figures of the analysis No. 2 become practically identical with those of No. 1; thus, the non-fatty solids become 7.65 per cent and the fat 44.45 per cent.

The milk of this species of the bottle-nosed whale is thus enormously rich in fat, whilst the non-fatty ingredients

are rather below than above the average of those present in the milk of ordinary mammals. The only other analysis of the milk of a *Cetacean* with which we are acquainted is that made by Prof. Purdie, of St. Andrews, of the milk of the porpoise, and which yielded the following very similar results (*Brit. Assoc. Report*, 1885, Aberdeen):—

Total solids..	58.89	per cent.
Water	41.11	"
Non-fatty solids..	13.09	"
Albumenoids	11.19	"
Milk sugar (?)	1.33	"
Fat	45.80	"
Mineral matter	0.57	"

The table below exhibits the composition of the milk of some of the commoner mammals.

We examined the ash of the whale's milk qualitatively, and found that it contained a large proportion of phosphoric acid. We also saponified the fat, and on treating the aqueous solution of the resulting soap with ether we obtained a small quantity of extract, which was, however, insufficient for further examination. On decomposing the soap with dilute sulphuric acid the resulting product proved to be only partially soluble in cold alcohol, a residue melting at 51° C. being left. This may possibly be spermaceti (m. p. 49° C.), which had escaped saponification, for, as is well known, it is only saponified very slowly. We were unfortunately unable to further investigate this interesting point owing to the material being exhausted.

A BRIEF SUMMARY ON PRACTICAL MANIPULATION.

By H. N. WARREN, Research Analyst.

Precipitation.

AMONG the numerous operations that are performed in the laboratory, none are perhaps oftener employed than that of precipitation. Many precipitates, not among the least of which noted for tedious and imperfect filtration may be mentioned those of barium sulphate and calcium oxalate, when recently precipitated, pass in considerable quantity through the pores of the paper. This may naturally be considerably retarded by employing both solutions at the boiling-point. But even then considerable risks are entertained, combined with a grievous waste of time. The addition of starch-paste has been recommended by several experts, but the same investigators omit to state what percentage of sulphide they obtain after ignition. I may mention, as an improvement, the following method:—Employ both the reagent and the solution containing the sulphate at an elevated temperature; at the same time introduce a few drops of ethereal solution of pyroxilin and mix well with the precipitate by stirring; the pyroxilin is at once set free, and, mixing intimately with the precipitate, allows of an immediate filtration. The separation of iron from manganese by means of sodium acetate is well known to be amongst the bulkiest precipitates obtainable for practical purposes; yet, if at the boiling temperature there be added to the precipitate finely powdered glass, it at once mechanically subsides, and, if dexterously performed, may be filtered

Average Percentage Composition, by Weight, of Milk from Various Mammals (Hoppe-Seyler).

	Woman.	Cow (summer).	Ewe.	Mare.	Bitch (meat-fed).	Sow.	Ass.	Buffalo.	Camel.	Hippo- potamus.
Water	87.24	86.48	83.30	91.15	71.21	81.80	89.01	80.64	86.34	90.43
Total solids	12.75	13.52	16.70	8.85	28.79	18.20	10.99	19.36	13.66	9.57
Casein	1.90	3.84	5.80	1.05	12.89	5.30	3.57	5.55	3.67	—
Fat	4.32	4.01	6.15	1.27	12.04	6.00	1.85	8.45	2.90	4.51
Sugar	5.97	4.93	3.96	5.75	1.82	6.07	5.05	4.52	5.78	—
Salts	0.28	0.74	0.66	0.37	1.63	0.83	0.52	0.84	0.66	0.11

and washed with impunity. As a third instance may be mentioned the effectual separation of precipitates occasioned during the manufacture of the pharmaceutical preparations, one of the most obstinate being the *Tinctura rhei* of the British Pharmacopœia.

A sample of this description which was lately presented to my notice has been, by the manufacturers, several times ineffectually passed through the variæ of commercial filters. The sample referred to, which was, when received, of a deep cloudy slate colour, due to suspended insoluble matter, was, after a short digestion with a small quantity of egg albumen, entirely freed from coherent matter by ordinary filtration. I may also mention that paper pulp distributed throughout the solution retains very perfectly any finely divided substances.

Incineration.

In cases where the total ash is required, such as the incineration of organic substances, among which may be mentioned the analysis of beet-sugar, so imperfect is the combustion of the organic matter, on account of the easily fusible salts which impregnate it, that an addition of a small quantity of H_2SO_4 is required in order to convert the inorganic salts present into sulphates, and thus render them less fusible, correction for increased weight being afterwards deducted.

The imperfect combustion of carbon when in contact with phosphates, especially the case of magnesium pyrophosphate, tends to increase errors; in which case I have observed several authors recommend the use of ammonium nitrate as a consumer of the carbon. I have, however, frequently used with success a plug of gun-cotton, omitting altogether a filter-paper.

Precipitation retarded.

Several organic acids or salts of the same are well known to retard the precipitation of metals when in solution. Among the most formidable are the tartrates and oxalates, also the citrates, which are not unfrequently unintentionally formed by the incautious filtration of strongly acid liquors through organic membranes; these may be altogether prevented by the employment of wool-glass; they are not, however, by any means the only acids that present a retarding action, one of the most opposing being hydroferrocyanic acid. So powerful is the action of this acid when in solution towards the salts of tin, so as not only to render the sulphide of tin unprecipitable, but even to immediately decompose it into the ferrocyanide after its formation.

Reading of Definite Quantities from Measured Flasks.

At the moment it may be desirous of denoting the exact capacity of a measured instrument, say, for instance, the reading from a measured flask, it not unfrequently happens that an accumulation of either froth or air-bubbles obliterate the dimension. These may be immediately expelled by the addition of one drop of alcohol.

(To be continued).

ON THE EXAMINATION OF ESSENTIAL OILS BY MAUMENÉ'S TEST.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

MAUMENÉ's test has been found so useful in conjunction with other methods of analysis as a means of detecting the presence of, and in some cases approximately estimating the proportion of, certain adulterants in fixed oils, e.g., linseed in rape oil and cotton-seed in olive oil, that it seemed to me worth while to apply the test to a number of essential oils which I have at hand.

I have already examined most of these oils by other methods, and published the results of my investigation in the CHEMICAL NEWS (vol. ix., p. 175).

For the benefit of those who are not very familiar with the mode of conducting Maumené's test, I may say that it consists in adding strong sulphuric acid to the oil under examination, generally in the case of ordinary fixed oils, in the proportion of 10 c.c. of acid to 50 grms. of oil, both being at the same initial temperature (preferably about 60° F.), stirring vigorously, and noting the highest point indicated by the thermometer.

In order to avoid loss of heat as much as possible, it is desirable that the operation should be conducted in a beaker surrounded by cotton-wool and packed in a somewhat larger vessel. The increase of temperature is much greater in the case of some fixed oils than of others, and depends upon a variety of circumstances, among others the nature of the oil itself, the strength of acid employed, the exact manner in which the acid is added, and the mode of stirring adopted. If these and other apparently minor details are not rigidly attended to, a considerable discrepancy may occur between duplicate experiments with the same sample of oil. Maumené's test can, therefore, only be regarded as an arbitrary one, and to obtain thoroughly satisfactory results every chemist should, whenever possible, examine samples of oil submitted to him for analysis under precisely the same conditions as a genuine specimen of the kind of oil in question. The results will then, in many cases, be of unquestionable value.

In the annexed table I give the figures obtained from all the essential oils which I have had the opportunity of examining by Maumené's test.

Table of Results.

Name of oil.	Rise of temperature in degrees F.
Aniseed	156
Bergamot—	
1st sample	186
2nd "	178
Cajeput—	
1st sample	91
2nd "	73
Caraway—	
1st sample	120
2nd "	136
Cassia—	
1st sample (pure)	102
2nd "	102
3rd " (adulterated with rosin)	147
4th "	158
5th "	184
6th "	173
7th "	200
Cedarwood—	
1st sample	55
2nd "	46
Cinnamon—	
1st sample	136
2nd "	150
Citron—	
1st sample	166
2nd "	166
Citronelle—	
1st sample	152
2nd "	152
Cloves—	
1st sample	122
2nd "	130
Eucalyptus—	
1st sample	97
2nd "	98
3rd "	82
Geranium (finest Spanish)	96
Juniper—	
1st sample (English)	144
2nd " (Foreign)	190

Name of oil,	Rise of temperature in degrees F.
Lavender, Mitcham—	
1st sample	120
2nd "	113
Lavender, Hitchin.. .. .	142
Lavender, French Petale—	
1st sample	112
2nd "	108
Lavender, Spike—	
1st sample	102
2nd "	162
Lemon—	
1st sample	152
2nd "	163
Lemongrass—	
1st sample	114
2nd "	104
Mace—	
1st sample	122
2nd "	116
Nutmeg—	
1st sample	118
2nd "	123
Orange—	
1st sample	152
2nd "	144
Pennyroyal—	
1st sample	84
2nd "	54
Peppermint, Mitcham—	
1st sample	67
2nd "	70
Peppermint, American—	
1st sample	72
2nd "	94
Peppermint, Japanese—	
1st sample	68
2nd "	78
Rosemary—	
1st sample	109
2nd "	134
Rue—	
1st sample	151
2nd "	182
Sage—	
1st sample	157
2nd "	157
Sassafras—	
1st sample	52
2nd "	89
Turpentine—	
1st sample	136
2nd "	160
3rd "	178
4th "	152
Thyme (red)—	
1st sample	108
2nd "	132
Verbena—	
1st sample	120
2nd "	104

A few words of explanation are necessary in connection with the preceding figures. In the first place I must state that owing to my having only a small quantity of most of the essential oils at my disposal, I decided to perform the test on 100 fluid grains of each sample, with certain exceptions hereafter mentioned. The carefully measured quantity was placed in a small glass beaker surrounded with cotton-wool in the manner previously described. The temperature of the oil having been taken, 20 fluid grains of strong sulphuric acid was added, and the mixture vigorously stirred with the thermometer until a point was reached at which the mercury ceased to rise, and the increase of temperature noted.

The acid which I employed in my experiments was ordinary pure sulphuric acid, previously heated for some time, and then kept in a well-stoppered bottle.

In the case of certain essential oils, addition of sulphuric acid causes so violent a reaction that the utmost care is required to obtain a satisfactory result, and even when every precaution is taken it is difficult to get reliable figures from some oils. This is owing to the frothing up or actual spitting which takes place when strong sulphuric acid is added to certain essential oils, especially to those of caraway, cinnamon, verbena, and lemongrass.

As I considered it advisable to use the same apparatus throughout this investigation, I found it necessary, in the case of the four oils above mentioned, to employ only 50 grains of oil and 10 grains acid; otherwise the action was so energetic as to cause part of the mixture to be violently ejected from the beaker. It is probable that by mixing these oils with olive oil (as is frequently done in the examination of linseed and fish oils by Maumené's test), before the addition of sulphuric acid, the reaction would be moderated and the results thereby rendered more accurate, but I have not applied this modification to any of them.

With regard to the oils of cassia, Nos. 1 and 2 are, I believe, pure. The remaining five samples are grossly sophisticated with various proportions of rosin. These, it will be noticed, give a much greater rise of temperature than the genuine oils. Maumené's test seems likely, therefore, to be useful as a confirmatory test for rosin in cassia and other essential oils when other methods of examination have indicated the presence of that adulterant.

It must be understood that in publishing these results I make no claim for their absolute accuracy, although the determinations were made as carefully as possible under the circumstances. The figures are only put forward now for the purpose of directing attention to the possibility of successfully applying Maumené's test to essential oils for the detection of certain impurities therein. Probably others, working under more favourable conditions as regards the quantity of essential oils at their disposal, will obtain somewhat different results to my own, for which reason I lay special stress on the necessity of each operator examining suspected samples of essential oils side by side with an undoubtedly pure specimen of the oil under consideration.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
January 24, 1890.

THE ANALYSIS OF CHROME IRON.

By R. FRESENIUS and E. HINTZ.

SOME time ago the authors had to execute the analysis of a chrome iron which, as it subsequently appeared, contained 61 per cent chrome, 28 per cent iron, and 9 per cent of chemically combined iron and graphite. As it was scarcely attacked by acid, and could only be dissolved by treatment with hydrochloric acid prolonged for weeks, the investigation presented difficulties which could only be overcome by degrees. It seems, therefore, interesting to describe the method which proved successful, and which we can therefore recommend.

1. Determination of Total Metals and of the Slag.

About 5 grms. of the chrome iron are placed in a porcelain boat, inserted into a tube of sparingly fusible glass, and heated for a long time in a current of desiccated chlorine gas free from air. The portion from the beginning of the tube to the boat is about 20 c.m., and that behind the boat 40 c.m. The end of the tube is bent at a right angle and leads into a Péligré tube, the other limb of the latter is connected with a Woolfe's bottle. The current of gas issuing from the latter passes

through two more Péligré tubes. The outer limb of the last is connected with a flask containing hydrate of lime in order to absorb the escaping chlorine. All these recipients contain water, but in the Woolfe's bottles only so much that the tube forming the connection between the first Péligré tube and the bottle leads not quite to the surface of the water.

The heat of the porcelain boat is raised very gradually, and that of the back part of the tube is regulated in such a manner that a relatively trifling quantity of the ferric chloride finds its way into the recipients, which are kept cool with water. The operation takes from three to four hours.

After the tube is cold, the recipients are disconnected, and in their place is joined on a Péligré tube containing a little water. The chlorine gas is then expelled from the tube by dry carbonic acid. Desiccated hydrogen gas, free from oxygen, is then passed through the tube, and both the boat and that part of the tube in which there is the greatest portion of sublimed chromic chloride is submitted to a gentle, but prolonged, ignition in order to convert it partly into chromous chloride, and thereby render it soluble in water. When cold the boat is drawn out. It contains the liberated carbon, the graphite, the small quantity of slag, chiefly particles of chrome iron which have escaped the action of the chlorine, also manganous chloride, and sometimes small quantities of iron and chromium chlorides. Its contents are treated with water, the undissolved matter is filtered off, washed, and dried, the filter is incinerated separately, and the residue is put in a porcelain boat, inserted in a glass tube, and heated in a current of dry oxygen, in order completely to burn the graphite. It is then heated in a current of hydrogen to reduce portions of iron oxide.

The boat is introduced into a new glass tube, arranged like that described for the first treatment with chlorine; the receivers which were formerly used are again connected, and the boat is again heated in a current of chlorine, free from air, until no further sublimate is formed, and the contents of the boat appear white. When cold, the boat is drawn out, its contents are heated in water, filtered, the undissolved slag is washed with hot water, dried, ignited, and weighed. If its weight is appreciable it is submitted to further analysis, according to the usual process.

The contents of the glass tube used in the second chlorine treatment are heated, as already indicated, first in a current of hydrogen. The contents of both tubes are heated in them with water, and a measured quantity of hydrochloric acid, of sp. gr. 1.1, and the solutions obtained are added to the contents of the receivers, and the liquid obtained on washing the slag. If the solution does not become clear even on long standing, or if a sediment appears it must be filtered. The contents of the filter are washed into a platinum capsule, the ash of the filter is added, the liquid is evaporated down to a small portion, dried up along with a mixture of equal parts sodium carbonate and potassium chlorate, heated to fusion, softened in water, and evaporated to dryness in a porcelain vessel with the addition of a little hydrochloric acid. The residue is moistened with a measured quantity of hydrochloric acid, of sp. gr. 1.1, water is added, any residue (*a'*) is filtered off, washed, dried, and laid aside. A filtrate here obtained is to be added to the main solution.

The flask containing such solution is then weighed in order to know the weight approximately, and a calculated quantity of pure sodium carbonate is added, *i.e.*, so much that there may remain in the liquid, in a free state, about 4 per cent of hydrochloric acid of sp. gr. 1.1, which can easily be effected as all the hydrochloric acid added has been measured.

The liquid thus prepared is submitted to prolonged treatment with sulphuretted hydrogen, at first at 70°, but afterwards in the cold. It is let settle for some time, the precipitate, which consists chiefly of sulphur, is filtered

off, washed with water, to which a little sulphuretted hydrogen water has been added, treated with hydrochloric acid containing a little bromine, filtered, washed, the excess of bromine is removed with ammonia, acidulated with hydrochloric acid, and the solution is again treated with sulphuretted hydrogen, as above. If no precipitate appears, the solution is added to the main liquid. If there is a precipitate, it is filtered off, and the filtrate is added to the main liquid. The precipitate, which may contain copper, lead, arsenic, antimony, and, in general, the metals of the V.th and VI.th groups, is treated by known methods for their separation and determination. The main liquid, which chiefly contains chromium and iron chlorides, and a moderate quantity of alkaline chlorides, is repeatedly evaporated to dryness in the water-bath to eliminate silica. The residue is moistened with hydrochloric acid, let stand for some time, mixed with water, filtered, and the precipitate (*a'*) is washed, dried, and the filter containing it and that containing the precipitate (*a*), if one exists, are incinerated together. If the ignited residue is white it is weighed, the silica is determined by volatilisation with hydrofluoric acid, any insoluble residue is fused with potassium disulphate, the melt is softened with cold water, and the solution is first tested for titanate acid by prolonged boiling. The solution, if it remains clear (or the filtrate if a deposit has been produced), is tested with ammonia, in order to be certain that there remain no oxides precipitable by this reagent.

If the ignited residue containing silica is not white it need not be weighed. It is fused with sodium carbonate in a platinum crucible, adding a little saltpetre. The melt is moistened with water, rinsed into a porcelain capsule, repeatedly evaporated to dryness with hydrochloric acid, treated with hydrochloric acid and water, filtered, and washed, the filtrate being added to the main solution. The precipitate is ignited, weighed, and treated with hydrofluoric acid, as above.

The main solution is treated with chlorine gas, or mixed with strong chlorine-water until it smells of chlorine, in order to convert the ferrous chloride into ferric chloride, any chromous chloride being at the same time converted into chromic chloride. The liquid is then subjected to prolonged heating in a porcelain capsule until the free chlorine is completely expelled, and the liquid is concentrated down to about 1 litre. It is let cool, introduced into a capacious boiling flask, a solution of sodium carbonate is added until the free acid is nearly neutralised, and to the clear liquid there is added pure barium carbonate ground up in water until a portion remains undissolved. It is repeatedly shaken up, let settle, the supernatant liquid is drawn off with a syphon, and the precipitate is completely washed by decantation. The liquids drawn off are filtered, the trace of precipitate remaining on the filter and the main bulk are dissolved in hydrochloric acid, and the liquid is made up exactly to 1 litre.

The precipitate consists chiefly of chrome and iron hydroxides, and barium carbonate. The liquid, filtered off, may contain manganese, nickel, cobalt, and zinc, if these metals were present in the chrome iron. It is evaporated down with the addition of some hydrochloric acid to about 500 c.c. The baryta is precipitated from the boiling liquid with dilute sulphuric acid, and is filtered and washed in order to free it from traces of the above-mentioned metals; it is placed in a small porcelain capsule with hydrochloric acid, evaporated down to a small quantity, mixed with water, filtered after some hours, and the filtrate is added to the liquid containing the manganese, &c. The whole is concentrated, almost neutralised, with ammonia, a sufficiency of ammonium acetate is added, and the solution is precipitated with sulphuretted hydrogen. The precipitate formed contains nickel, cobalt, and zinc, if present. These metals are separated by the ordinary methods.

The manganese, which is in the filtrate, is precipitated at a boiling heat by bromine and ammonia; but as the

hydrated peroxide thus obtained contains alkali it is dissolved in hydrochloric acid, the solution precipitated with ammonium sulphide after the addition of ammonia, and the manganese determined as manganous sulphide.

There now remains the solution containing the iron and the chrome, which has been brought to the volume of 1 litre. Of this, 200 c.c. are evaporated down to a small residue to expel the greater part of the hydrochloric acid; water is added, and it is raised almost to a boil with the cautious addition of dilute sulphuric acid in order to remove baryta. After long standing the barium sulphate is removed, placed in a porcelain capsule, covered with hydrochloric acid, which is then evaporated down to a small residue; water is added, and after some hours it is filtered and washed with water, repeating this hydrochloric treatment twice more in the same manner in order to remove all traces of ferric and chromic oxide which may adhere to the barium sulphate.

All the liquids thus filtered off from the barium sulphate are evaporated first in a porcelain capsule, and then in a small platinum capsule, down to a small residue. Pure sodium carbonate is then cautiously added up to a slight excess, and then 5 grms. of a mixture of equal parts of sodium carbonate and potassium chlorate. The mixture is completely dried, and gradually heated to fusion. When cold, the melt is treated with hot water, filtered, washed until the washings run off quite colourless; the filter, in which there is a portion of the ferric oxide, is dried and incinerated in the platinum capsule containing the remainder of the ferric oxide; 4 grms. of the mixture of sodium carbonate and potassium chlorate are added, the whole is melted, and the melt, when cold, is treated with hot water until everything soluble is removed. In these operations the use of glass vessels must be avoided, as they are attacked by the strongly alkaline liquids; vessels of platinum or of porcelain are used in preference.

If the final filtrate is colourless, or has only a very faint yellow tint, we have all the ferric oxide in the residue and all the chrome in solution. The ferric oxide is dissolved in hydrochloric acid, precipitated with ammonia, and determined as usual. After it has been weighed, it is dissolved in fuming hydrochloric acid, and the (generally trifling) residue of silica derived from the vessels is determined and deducted from the weight of the ferric oxide. The solution of the ferric chloride is poured into pure hot potassa lye in a platinum capsule to find if any alumina is dissolved; if so, it is determined and deducted from the ferric oxide.

The solution containing the chrome as an alkaline chromate is acidified with hydrochloric acid, and ammonia is added until the liquid is just alkaline. If there appears at once, or after standing, a white flocculent precipitate, it is filtered off, washed, and weighed. It may be alumina, aluminium phosphate, a residue of silica or of titan acid, or a mixture of these bodies. Its weight is first determined, and it is then fused with potassium disulphate, and treated by known methods to determine its nature.

The liquid which remained clear on the addition of ammonia, or the solution filtered from the above white precipitate, is mixed with a sufficiency of hydrochloric acid, alcohol is added, and the whole is heated in a porcelain capsule until all the chrome is converted into chloride. The chrome is then precipitated with ammonia as hydroxide, and determined as usual. If the chrome-iron contained phosphorus, and if the phosphoric acid thence arising has not been completely eliminated along with alumina, it goes down along with the chromium hydroxide. The quantity of phosphoric acid thus weighed along with the chromic acid must be deducted from the weight of the ignited precipitate before the quantity of chromium can be calculated.

2. Determination of total Carbon, Phosphorus, and Sulphur.

Five grms. of the mineral are again treated in a current

of chlorine precisely as described under 1. The contents of the boat, with the addition of a little solution, are digested for a long time with hydrochloric acid and water, and decanted through an asbestos filter. If particles of chrome-iron still appear, the undissolved part must again be heated in a current of chlorine free from air, until there is no further formation of a sublimate. In any case, the carbonised residue is washed until the washings no longer give the reaction of chlorine, and the contents of the filter are then treated in the ordinary manner with chromic and sulphuric acids in order to convert the entire quantity of carbon into carbonic acid for its determination.

The contents of all the receivers which contain all the sulphur and phosphorus in the state of phosphoric acid are evaporated to dryness along with some sodium chloride in order to separate silica. The residue is heated with hydrochloric acid and water, filtered, nearly neutralised with ammonia, barium chloride is cautiously added to the clear solution so as to throw down the sulphuric acid. It is let settle for some time, the barium sulphate is filtered off, purified by evaporation with hydrochloric acid thrice repeated, washed with water, as directed under 1, weighed, and the sulphur present in the chrome-iron is thus calculated.

The solution filtered off from the barium sulphate, together with the washings, is evaporated down with repeated additions of nitric acid, until all the hydrochloric acid is driven off. The phosphoric acid is then separated by means of molybdic acid, determined as usual, and from the results the proportion of phosphorus in the chrome-iron is calculated. If the mineral is arseniferous, the washed ammonium-magnesium phosphate is dissolved in hydrochloric acid, and any arsenic acid existing in the precipitate is removed by means of sulphuretted hydrogen. From the filtrate, after concentration, the ammonium-magnesium phosphate is reprecipitated by means of ammonia and a little sodium-ammonium phosphate.

3. Determination of Graphite.

Ten grms. of the sample are digested for weeks with hydrochloric acid—often renewed—until all the iron and all the chrome are dissolved, and the undissolved matter does not follow a magnet held underneath the flask. All the hydrochloric acid poured off is passed through an asbestos filter, the residue of graphite is washed with water, potassa-lye, alcohol, and ether, and treated with chromic and sulphuric acids, as in 2, to determine its carbon. On deducting its weight from that of the total carbon we find the carbon in chemical combination.—*Zeitschrift für Analytische Chemie.*

THE ESTIMATION OF MINUTE QUANTITIES OF GOLD.*

By Dr. GEORGE TATE, F.I.C., F.C.S.,
Principal at the College of Chemistry, Liverpool.

(Concluded from p. 55).

SINCE it might be urged against the utility of the microscopic estimation of gold, that the ordinary crucible or "pot" method of assaying ores, might be incapable of enabling the assayer to isolate the one ten-thousandth of a grain, or that the losses incidental to cupellation, parting, collection, and fusion of the gold, were together in excess of that weight, I have conducted a large number of experiments, which tend to prove that, with care, exceedingly minute quantities of gold are capable of isolation, and that the percentage loss of metal is extremely small. A few of these experiments are here recorded.

* A Paper read before the Liverpool Polytechnic Society, November, 1889.

Distribution of Gold in Lead Alloys.—To determine that my method of obtaining standard gold prills from lead alloys was not appreciably affected in accuracy by want of uniformity in the distribution of the gold throughout the lead, I prepared an alloy of gold with assay lead. After allowing the ingot of metal to slowly cool, portions of 2 grms. (30 grains) were taken from the top, centre, and bottom of the ingot, and separately assayed for gold.

The prills of parted gold measured respectively 15.9, 16.4, and 17.0 divisions, indicating 0.30, 0.32, and 0.36 m.grms., or 0.0046, 0.0049, and 0.0053 grain of gold. When the gold-lead alloys employed for preparing standard prills are well flattened, one may hence feel assured of the uniformity of the alloy.

Loss in Parting.—Gold prills varying from 0.0001 to 0.002 grain in weight according to measurements with the microscope were alloyed with various proportions of silver, parted from this metal, and then collected and fused into beads. In the majority of cases the prills were repeatedly alloyed and parted.

Parting tests A and B:—

Gold prills.	Measure ($\frac{1}{4}$ inch).	Weight in m.grms.	Parting loss in m.grms.
Original	43	0.0772	
1st parting	43	0.0772	nil.
2nd "	40	0.0621	0.0151
3rd "	37	0.0491	0.0130
Original	43	0.0772	
1st parting	41	0.0670	0.0102
2nd "	40	0.0621	0.0049
3rd "	36	0.0452	0.0169
4th "	35.8	0.0445	0.0007
5th "	34.5	0.0388	
6th "	35	0.0416	0.0029

Total loss in 3 partings, A 36 per cent.

" " " B 46 "

Average loss for 1 parting, A 12 "

" " " B 8 "

Parting tests C:—

Original gold	0.000100 grain.
Gold after 1st parting	0.000088 "
Gold after 2nd "	0.000072 "
Loss in 2 partings	0.000028 " or 28 p. c.

Parting tests D:—

Gold taken	0.000100 grain.
After cupellation with large excess of silver and 100 grains lead, and parting twice	0.000075 "
Loss in 2 partings	0.000025 " or 25 p. c.

In the above tests the silver was in each case in excess of the quantity necessary for parting, but had not been weighed.

In the following series silver, in the form of a lead alloy, was added in definite amount. (See next column).

After each parting in these two series the silver solution was filtered through good filter paper. The paper was finally assayed for gold and found to contain 0.093 m.grm. gold, showing that 0.0196 m.grm. gold was presumably in the acid solution, and that one-half of the loss only was due to minute particles of float-gold being mechanically carried away in the washing.

Parting test G.—Gold 0.0193 m.grm., parted from 2500 times its weight of silver (0.05 grm.), yielded:—

Gold	0.0143 m.grm.
Loss on parting	0.0050 " or 25 per cent.

Parting test H.—Gold 0.0126 m.grm., parted from 16,000 times its weight of silver (0.200 grm.), yielded, after a second parting from a small excess of silver, necessitated by want of purity of the first prill:—

Gold	0.0071 m.grm.
Loss on parting	0.0055 " or 43 per cent.

Parting tests E:—

Parting No.	Gold measure 1-in. objective.	Parted from sil- ver. M.grms.	Weight of gold. M.grms.	Loss in weight. M.grms.	Loss per cent.	Ratio gold: sil- ver.
—	8.75	—	0.0491	—	—	—
1	8.75	0.25	0.0491	0	0	1:5
2	7.9	0.25	0.0350	0.0141	28	1:5
3	8.0	0.25	0.0374	0	0	1:7
4	8.0	0.50	0.0374	0	0	1:13
5	7.5	1.0	0.0309	0.0065	17	1:27
6	6.9	1.0	0.0239	0.0070	22	1:30

Parting tests F:—

—	9.9	—	0.0708	—	—	—
1	9.8	0.25	0.0685	0.0023	3	1:3.5
2	9.7	0.25	0.0662	—	—	1:3.5
3	9.8	0.25	0.0685	0	0	1:3.5
4	9.7	0.50	0.0662	0.0023	3	1:7
5	9.2	1.0	0.0571	0.0091	15	1:15

Average loss for each parting 8 per cent

Maximum loss 28 "

Minimum loss 0 "

Total loss on the combined weights
of the original prills 0.0389 m.g. or 32%

From these and other parting tests I conclude that the average loss in parting the one-thousandth of a grain of gold from silver is about 5 per cent; in parting the one-tenth-thousandth of a grain, between 10 and 20 per cent; that the loss increases with the proportion that the silver bears to the gold, and that this loss is partly mechanical and partly owing to the solvent action of the nitric acid upon the gold when in presence of silver or of products of the reduction of the nitric acid.

The variations that I have noted in the loss on parting I attribute either to the variable molecular conditions of the alloys (dependent possibly upon rates of cooling) or to variations in the heating during the action of the acid, giving rise to variable products of reduction of the acid. Experiments are in progress to determine more accurately the cause of the solvent power of nitric acid upon minute quantities of gold.

Loss in Cupellation.—That gold suffers at most only an infinitesimal loss when cupellated with pure lead (free from silver) is satisfactorily proved by the accuracy with which the standard prill, the one-millionth of a grain, has been obtained by cupellation.

I will here briefly detail four experiments that show the gold suffers no appreciable loss during cupellation with antimony and copper.

Portions of gold, each 0.1 m.grm. (0.00154 grain), were alloyed with 15 grms. (300 grains) of lead containing a trace of silver, and cupellated separately with—

- (1). 0.5 grm. (8 grains) copper.
- (2). 0.5 " (8 ") antimony.
- (3). 2 " (30 ") copper.
- (4). 0.5 " (8 ") antimony after scorification.

After parting, the residual gold was estimated to be in m.grms. respectively 0.098, 0.111, 0.097, and 0.100 in the four experiments.

Loss of Gold in Extraction from Siliceous Ores.—To enable me to experiment with ores containing proportions of gold equivalent to 2 dwts. or less per ton (0.0003 per cent), I obtained from a rich gold ore siftings through a very fine sieve that gave fairly constant results on assay. This ore, in weighed quantity, was mixed with a large excess of sand and substances commonly occurring in quartz ores that were themselves free from gold. The mixtures thus prepared, representing poor gold ores of

Total weight of ore, grms.	Weight of gold in m-grms. introduced according to average.	Average content of gold in grains per ton.	Constituents of ore other than gold.	Lead alloy from crucible, in grms.	Gold obtained in m-grms.†	Gold obtained in grains per ton.	Apparent error in weight of gold.	Apparent error in grains per ton.	Remarks.
25	0.084	53	Silica.	17	0.103	63	+0.019	+10	
25	0.084	53	"	9	0.060	37	-0.024	-16	10 grms. only of litharge used.
60	0.084	22	"	20	0.085	23	+0.001	+1	
15	0.084	87	Silica, Arsenic, Copper.	10	0.103	106	+0.019	+19	2½ grms. arsenical copper precipitate.
15	0.084	87	Silica, Zinc, Sulphide.	11	0.093	97	+0.009	+10	Zinc blende, 2½.
20	0.084	65	"	23	0.093	73	+0.009	+8	Zinc blende, 5 grms., calcined.
15	0.093	97	{ Silica, Copper, Antimony, Sulphur. }	20	0.094	98	+0.001	+1	2½ grms. ore containing chiefly copper, antimony, and sulphur.

known content of gold, were assayed by the crucible method.*

The fine rich ore gave the following results on assay; in the first three tests the gold obtained was weighed, in the last six tests the gold was measured:—

5 grms. ore gave gold	4.1 m-grms.	or 0.082 p. c.
2	"	1.7
1	"	0.8
0.5	"	0.394
0.5	"	0.442
0.1	"	0.0885
0.1	"	0.0938
0.1	"	0.0980
0.05	"	0.0353
		averaging 0.0877

I concluded that a fair average for the gold in 0.1 grm. would be 0.084 m-grm., with probable minimum and maximum amounts respectively of 0.0788 and 0.0980.

By means of 0.1 grm. gold, according to the above average, to the amount of 0.084 m-grm. was added to various materials, which were then assayed with the results given in Table above.

In the second assay the gold was purposely separated under disadvantageous conditions, only 9 grms. of lead being produced in the fusion, but even here 70 per cent of the total gold was isolated.

The above results indicate that one-tenth of a m-grm. or 14 thousandths of a grain of gold can be isolated from weights of siliceous ore, ranging from 15 to 60 grms. or from 200 to 1000 grains in weight, even in the presence of copper, arsenic, antimony, zinc, and sulphur compounds.

Finding that a millionth of a grain of gold could be cupellated from lead without loss, I successfully attempted the recognition of the millionth of a grain of the metal, when in alloy, with a trace of silver. The parting was conducted with a small drop of nitric acid upon a microscope slide. The black sponge of gold that was left was distinctly visible under the microscope. Washing was performed by adding drops of water and carefully applying to the edge of the liquid small pieces of bibulous paper. By watching the sponge, this separation of the silver solution can be successfully performed without loss of

* It would appear from my own observations and from the experience of other assayers that the method of fusion with litharge in a crucible gives results of greater accuracy than the method of scorification with lead. This is probably due to the difference in form of the two vessels, and no doubt accounts for the greater favour buyers show towards the latter method.

† The weights of gold in these test assays were estimated by comparison with 0.1 m-grm. standards only. These standards were some of the earliest prepared, and were cupellated upon ordinary (somewhat rough) cupels. The estimate of diameters of 0.1 m-grm. standards since prepared is such as to make these weights of gold about 12 per cent less than those given. The same error applies to the last four tests in the preceding table. Reference is made, and this chiefly to impress the necessity for employing smooth cupels for obtaining pills.

gold. After drying the slide it was again brought upon the stage of the microscope, and the gold picked up by means of a minute piece of pure lead fixed upon the point of a stout needle. By cupellation a distinct visible bead of yellow gold was obtained. It is thus possible, under favourable conditions, to recognise in a complex mixture even the *millionth of a grain of gold*.

This method of working under the microscope should be of value to geological science, by permitting of the search for gold in rocks neighbouring gold deposits, and thus throw light upon the "origin of gold in veins and lodes."

Data Useful in Assaying.

Parts of ore.	Per ton.		
	ozs.	dwt.	grains.
100 yielding 0.00001 part of gold =	0	0	1.5
" " 0.0001 " "	0	0	15.6
" " 0.001 " "	0	6	12
" " 0.01 " "	3	5	8
" " 0.1 " "	32	13	8
" " 1.0 " "	326	13	8
24 grains .. equal to 1 pennyweight	} troy.		
20 pennyweights .. 1 ounce			
1 milligram. (m.g.) equal to 0.0154 grain.			
1 thousandth grain .. 0.0648 milligram.			

Table of Cubes.

Number.	Cube.	Number.	Cube.
1.0	1	10.0	1000
1.5	3.3	10.5	1157
2.0	8	11.0	1331
2.5	15.6	11.5	1521
3.0	27	12.0	1728
3.5	42.9	12.5	1953
4.0	64	13.0	2197
4.5	91	13.5	2460
5.0	125	14.0	2744
5.5	166	14.5	3049
6.0	216	15.0	3375
6.5	275	15.5	3724
7.0	343	16.0	4096
7.5	422	16.5	4492
8.0	512	17.0	4913
8.5	614	17.5	5359
9.0	729	18.0	5832
9.5	857	18.5	6332

For figures that are not given in the table, and that are higher than 8, approximate cubes may be obtained by taking proportionate differences.

For cubes of numbers higher than those given, many can be obtained by taking the cube of half the figure and multiplying by 8. Thus, the cube of 24 will be 8 times

were partial loss by volatilisation, either during the ignition in hydrogen, or in subsequently recovering the potassium chloride from solution. The quantities of material used were smaller than is probably desirable.

c. *Experiments of Levol, 1850.**—A weighed quantity of gold was dissolved as auric chloride, the metal reduced from the solution by means of sulphur dioxide, and the sulphuric acid formed was determined as barium sulphate. In two experiments, reported as giving exactly the same result, 1 grm. of gold gave 1.782 grms. of barium sulphate. Hence, if Ba be taken = 136.86, S = 31.98, and O = 15.96, we have, for the atomic weight of gold, the number 195.86.

Of the sources of error to which this method is liable, probably the most important are atmospheric oxidation of sulphurous to sulphuric acid and imperfect washing out of soluble compounds of barium from the barium sulphate. Both would tend to give too low a result for gold.

For all these earlier experiments details are wanting as to the exact mode of purification of the gold and other materials used, and in the weighings there appears to have been no correction introduced for atmospheric buoyancy; the results doubtless represent apparent, not absolute weights.

(There is also to be quoted the statement of Julius Thomsen,† that he found in hydrogen bromate ($\text{AuBr}_3 \cdot \text{HBr} \cdot 5\text{H}_2\text{O}$) 32.11 per cent of gold and 52.00 per cent of bromine, from which he concluded that Au = probably about 197. Taking Br = 79.76, and calculating from the ratio of Br : Au, the number is 197.01).

Recent Careful Determinations of the Atomic Weight of Gold.

a. *Experiments of Gerhard Krüss, 1886.*‡—The author has described in detail the means resorted to for the preparation of pure metallic gold, and especially for its separation from silver and the metals of the platinum group, with an account of the spectroscopic examination of the gold employed. He has then given a full account of:—(a) His determinations of the gold and chlorine (the former reduced by a stream of sulphur dioxide; the latter precipitated and weighed as silver chloride) in a neutral solution of auric chloride, prepared by the action of water on the so-called auro-auric chloride (Au_2Cl_4),§ itself, prepared by the direct action of chlorine on metallic gold; (b) Like determinations of gold and chlorine in sublimed auric chloride, made by direct action of the elements on each other with careful regulation of the temperature. (c) Determinations of the gold in a weighed quantity of potassium auribromide (KAuBr_4), the metal in some experiments reduced from a solution of the salt by sulphurous acid, in others reduced from the dry salt by heating in a stream of hydrogen; (d) Determinations of the gold and bromine (the former thrown down by sulphurous acid; the latter precipitated as silver bromide) in the same salt, potassium auribromide; (e) Determinations of the loss of weight (representing 3 atoms of bromine for 1 of gold) undergone by heating potassium auribromide gradually to 320° C., towards the end, in a stream of hydrogen; (f) Determinations of the quantity of potassium bromide recovered from the residue left in the experiments of (e) by treatment of this residue with water, separation of the metallic gold, careful evaporation of the liquid, and final cautious heating of the potassium bromide over a free flame. In the experiments of series a account was taken of the somewhat different processes of purification of the gold used, but no corresponding

differences being observable in the results obtained, no further record was made in the remaining series of the history of the gold used in these.

After correction of the weighings for atmospheric buoyancy in such cases as seemed to the author to involve a correction worth noticing, the following results were calculated from the figures obtained, these figures agreeing in general closely with other in each series:—

Series.					
a.	Mean of 8 experiments. Atomic wt. of gold = 196.622				
b.	"	4	"	"	" = 196.143
c.	"	9	"	"	" = 196.741
d.	"	5	"	"	" = 196.743
e.	"	4	"	"	" = 196.619
f.	"	4	"	"	" = 196.620

Leaving out the results of series b, on the ground of the very small quantity of sublimed auric chloride available, and the considerable discrepancy of one of the results (that in which most material was used) from the rest, the author calculates from the remaining 30 experiments the general mean 196.669; but, taking into account the greater or less closeness of agreement of the figures obtained by the several methods, he comes to the conclusion that 196.64 may better be assumed as the true atomic weight of gold. In these calculations Ag was assumed = 107.660, Cl = 35.368, Br = 79.750, and K = 39.040.

As regards possible sources of constant error in Krüss's experiments, it may be observed that—

1. In series b very small quantities of sublimed auric chloride were used—the whole amount available for all four experiments being only about seven-tenths of a grm.—and it is probable that a little free chlorine may have been physically retained by the chloride in spite of the long-continued passage over it of dry air. The experiment in which the largest quantity of material was used gave the atomic weight = but 194.79. On these grounds the author himself excludes the series from consideration in calculating his general mean.

2. In series c, d, and e the evidence is pretty strong, but perhaps not conclusive, to show that potassium auribromide can be rendered absolutely dry by exposure to air in a vessel containing phosphorus pentoxide, either at ordinary or higher temperatures, without, at the same time, undergoing any loss of bromine. The attainment of constant weight by the salt does not positively prove the entire removal of water. If moisture were retained the atomic weight of gold found would be brought out lower than it should be.

3. Krüss himself observed that in all cases in which he dissolved potassium auribromide in water, a small residue of metallic gold was left, and, determining in a single experiment the amount of this (about 0.05 per cent), he used it as a correction for all his results. As pointed out by Thorpe and Laurie,* this partial decomposition of the salt was probably due to the action of dust from the air. If the results obtained from the solution were used, without any correction, to establish the atomic weight of gold, the tendency would, of course, be to a value lower than the truth. Although the correction introduced is small, it can hardly be supposed that it should be taken as constant in amount in all the experiments.

4. In series e it may be questioned whether traces of potassium bromide may not have been volatilised at the highest temperature used, or the residual potassium bromide may not have, to a small extent, exchanged bromine for oxygen while heated in air (before the use of the stream of hydrogen), the latter change being one to be guarded against whenever haloid salts are strongly heated in the presence of free oxygen. The tendency in both cases would be to a lower atomic weight for gold.

5. In series f there was risk of slight loss of potassium bromide during filtration and evaporation of its solution,

* *Annales de Chimie* [3], vol. xxx., p. 355.

† *Journ. Prakt. Chem.*, vol. xlii., 1876, p. 345.

‡ *Liebig's Annalen*, vol. cxxviii., p. 30; and separate publication, G. Krüss, "Untersuchungen über das Atomgewicht des Goldes," München, 1886.

§ Krüss has, in a later paper (*Berichte Deutsch. Chem. Gesell.*, vol. xx., p. 2634) denied the existence of auro-auric chloride as a definite compound, but admits that the substance so described by Julius Thomsen yields, on treatment with warm water, a solution of pure neutral auric chloride, with separation of metallic gold.

and during exposure of the salt to the heat of a free flame, when there might possibly have been again slight replacement of bromine by oxygen, thus causing the atomic weight sought to come out too high, or else, on the other hand, risk of imperfect drying, which would give too low a value for the atomic weight in question.

On the whole it seems probable that the tendency of most of the constant errors to be suspected in connection with Krüss's experiments—experiments carried out with remarkable patience, skill, and apparent freedom from merely "fortuitous" errors—was in the direction of an atomic weight for gold somewhat below, rather than above, the true value.

B. Experiments of Thorpe and Laurie, 1887.*—In these experiments potassium auri-bromide was used, and determinations were made:—*a.* Of the weight of the residue left on heating the salt over a Bunsen flame till bromine ceased to be given off (this residue consisting of metallic gold and potassium bromide), and the weight of the gold left by such residue after all potassium bromide had been washed out of it by water; *b.* Of the weight of silver necessary to be added as nitrate to the solution of potassium bromide obtained in *a* in order to just precipitate the bromine present; *c.* Of the weight of the silver bromide so precipitated. All suitable experimental precautions seem to have been taken, and the weighings were corrected for atmospheric buoyancy. The individual results in each series agreed with each other even more closely than in Krüss's research.

The results obtained were as follows, using in calculation the numbers $Ag = 107.66$, $Br = 79.75$, and $K = 39.03$:—

Series.

<i>a.</i>	Mean of 8 experiments.	Atomic wt. of gold	= 196.876
<i>b.</i>	" 9 "	" "	= 196.837
<i>c.</i>	" 8 "	" "	= 196.842

The general mean of these values, giving equal weight to the different series, is 196.852.

As regards possible sources of constant error specially belonging to these experiments, it is to be noticed—

1. There is an advantage, as observed by the authors themselves, over the greater part of the experiments of Krüss in the nature of the relations employed not requiring that the potassium auri-bromide should be perfectly dry, the exact quantity of the original salt not needing, in fact, to be known.

2. In series *a* it is conceivable that there might have been slight volatilisation of potassium bromide, or interchange in it to a small extent of bromine for oxygen, during the heating of the original salt, or retention of traces of potassium bromide by the metallic gold when washed—the latter but little probable. Any of these defects, if existing, would cause the method to give a higher value for Au than the true one.

3. In series *b* the probability seems to be in favour of not quite the whole of the original potassium bromide being actually used, and minute loss of silver solution having perhaps occurred, so that rather more of this solution was counted as used than the true quantity. If so, the former defect would tend to raise, the latter to lower, the atomic weight of gold.

4. In series *c*, in view of the evidence adduced to prove complete drying of the silver bromide, it is more likely that its weight as obtained was below, rather than above, the truth. Hence we should suspect, if any constant error exist, that it would rather tend towards an unduly high value for Au.

On the whole, there seems to be less reason to fear sources of constant error of any considerable amount in connection with the experiments of Thorpe and Laurie than with those of Krüss, and the drift is in the opposite direction, tending rather to give too high than too low a value for the atomic weight to be determined.

It should be mentioned that Krüss* has claimed that in the potassium auri-bromide used by Thorpe and Laurie there was probably as much free gold as he considered to exist in the salt used by himself, and on this assumption has calculated that the three series of experiments by the English chemists should, if corrected on this account, lead to the numbers 196.616, 196.559, and 196.575 respectively for Au. From this conclusion the latter chemists altogether dissent,† and express their confidence that in none of the preparations used by them was there free gold sufficient to account for the difference between their own results and those of Krüss.

(To be continued).

OBITUARY.

THE LATE M. G. A. HIRN.

M. G. A. HIRN, correspondent of the Physical Section of the Academy of Sciences, died at Colmar on January 14, in his seventy-fifth year. He was carried off by the prevailing epidemic. The deceased *savant* was born at Logelbach, August 21, 1815, and was nominated as a correspondent of the Academy in the Physical Section in 1867. In his twenty-sixth year, in conjunction with his elder brother, Ferdinand, he undertook the direction of the extensive tissue-printing works of Haussmann, Jordan, and Co., at Logelbach. He made a series of remarkable investigations on superheated steam, the use of steam-jackets, the exchange of heat through metal walls, &c. He also undertook studies on lubricating oils, and introduced the use of mineral oils which had been considered unfit for lubrication. One result of his labours was to make him a fervent believer in the mechanical theory of heat. He installed, in the region of the Vosges, posts of meteorological observation at different altitudes, and the results obtained formed the substance of several communications to the Academy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 3, January 20, 1890.

The Different States of Graphitic Carbons, and on the Corresponding Chemical Derivatives.—M. Berthelot and P. Petit.—The study of the isomerism of simple bodies, otherwise called allotropy, is one of inquiries which enable us to penetrate furthest into the constitution of matter and of the chemical elements, and that of the allotropies of carbon is particularly interesting. In examining the multiple states of carbon one of the authors has sought to explain them by the polymeric condensations of the true element designated by that name, which has no permanent existence in the free state of a simple molecule. The graphites in particular, when oxidised by the moist way at a low temperature, form ternary compounds, one of the terms of which have been discovered by Brodie. M. Berthelot has since shown that there are several different states or graphites chemically distinct, forming each a special graphitic oxide, which produces a corresponding hydrographitic and pyrographitic oxide, and may be reproduced from them with

* *Chem. Soc. Journ.*, June, 1887, p. 565, and Dec., 1887, p. 866.

* *Berichte Deutsch. Chem. Gesell.*, vol. xx., p. 2365.

† *Chem. Soc. Journ.*, Dec., 1887, p. 868.

the speciality of its primitive characters. There are three distinct graphitic oxides; that of the graphite of cast-metal contains 62.7 per cent of carbon; that of amorphous graphite (plumbago) contains 56.2 per cent; and that of electric carbon 51.9 per cent. The comparison may be made by admitting that one and the same proportion of oxygen, such as O_{16} , is combined in the three bodies to carbons differently condensed, i.e., $2C_{28}$ in the first, $2C_{22}$ in the second, and $2C_{16}$ in the third. Each graphite would thus represent a different simple radicle, which is permanent in its combinations, as Brodie has already shown for one of them.

Combustion- and Formation-Heat of the Graphitic and Pyrographitic Oxides.—M. Berthelot and P. Petit.—A thermo-chemical paper, which does not admit of useful abstraction.

Remarks on the Formation of Nitrates in Plants.—M. Berthelot.—M. Heckel has shown that the caffeine contained in the seeds of Kola disappears progressively along with the formation of potassium nitrite. M. Lundström has also shown that saltpetre takes its rise in special organs of the coffee and other trees. These observations seem to throw a new light on the formation of saltpetre in the Amaranths observed some years ago by M. André and M. Berthelot. These facts establish the likeness and the connection between the life of microbia inhabiting the soil and that of microbia which inhabit plants, and which often there intensify their specific chemical activity.

The Combinations of the Alkaline Metals with Ammonia.—H. W. Bakhuis-Roozeboom.—This paper constantly refers to an accompanying diagram.

The Absorption of the Ultra-Violet Rays by Certain Organic Substances belonging to the Fatty Series.—J. L. Soret and A. A. Rilliet.—The author communicate the conclusions to which they have been led in researches on the absorption of the ultra-violet rays. Many of their results agree with those of MM. Hartley and Huntington (*Phil. Trans.*, 1879, Part I.). The alcohols of the fatty series are generally very transparent for ultra-violet rays. They estimate that the degree of absorption of these rays constitute a very delicate means for recognising the purity of organic bodies.

The Refractive Powers of Double Salts in Solution.—E. Doumer.—In general the molecular refractive power of a salt, whether simple or double, is proportional to the number of valencies of the metallic portion of the salt. The facts observed afford a means of determining the molecular refractive power of simple salts which are not easy to prepare in a state of purity, but which are capable of yielding double salts, soluble and easily purified.

The Substitution-Derivatives of Ammonium Chloride.—J. A. Le Bel.—Certain chemists consider this salt as a chloride of nitrogen pentahydride, ascribing to the five atoms linked to the nitrogen a part exactly identical. Others consider it as an ammonium hydrochlorate. The author's views do not admit of abridgment.

Reactions between Salts of Copper and Metallic Cyanides.—Raoul Varet.—The haloid salts of copper undergo double decomposition with all the cyanides. The oxalates are without action upon the mercury and silver cyanides only.

The Different Dextro-, Levo-, and Racemic Bornylphenylurethanes, and on the Isobornylphenylurethanes.—A. Haller.—Not adapted for useful abstraction.

The Physiological Action of Selenious Acid.—C. Chabré and L. Lapique.—The organic sulphides yield neutral oxides, whilst the oxides of the selenides of the fatty series are strongly basic. A dose of selenious acid a little above two-thousandths is necessary to prevent the fermentation of beef-broth under the action of the microbia of the atmosphere. Sulphites, if injected into the blood

of an animal, are transformed into sulphates, which possess no poisonous action. The selenites are not oxidised under these conditions. An aqueous solution of selenious acid accurately neutralised with soda is fatal to dogs if introduced in the proportion of 3 m.grms. per kilo. of the weight of the animal. The heart is arrested in systole, and all the viscera are intensely congested.

MISCELLANEOUS.

Royal Society of New South Wales.—Original Researches.—The Royal Society of New South Wales offers its Medal and a Money Prize for the best communication (provided it be of sufficient merit) containing the results of original research or observation upon each of the following subjects:—

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New Process for the Preparation of Alumina and Alkaline Aluminates.—Dr. K. J. Bayer.—The author's process is based upon the fact that a solution of sodium aluminate (obtained by treating bauxite with sodium carbonate or sodium sulphate and carbon) is decomposed on agitation with alumina.—*Chemiker Zeitung*.

NOTES AND QUERIES.

*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Phosphorescence.—Will any of your readers kindly inform me of the cause of the gleam of light seen when some finely powdered limestones are projected on to a heated surface; as, for example, into a platinum crucible heated so as to show just dull red in the dark? I have noticed this in the case of a great number of limestones, the gleam of light varying much in intensity and colour, from white to dark yellow and yellowish green.—W. J. COOPER.

MEETINGS FOR THE WEEK.

- MONDAY, 10th.**—Medical, 8.30.
Society of Arts, 8. "The Electro-magnet," by Silvanus P. Thompson, D.Sc., M.I.E.E.
- TUESDAY, 11th.**—Royal Institution, 8. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
Institute of Civil Engineers, 8.
Photographic, 8. (Anniversary).
Royal Medical and Chirurgical, 8.30.
Society of Arts, 8. "Cast-iron and its Treatment for Artistic Purposes," by W. R. Lethaby.
- WEDNESDAY, 12th.**—Society of Arts, 8. "Modern Improvements in Facilities for Railways: Travelling," by George Findlay.
Microscopical, 8. (Anniversary).
Pharmaceutical, 8.
- THURSDAY, 13th.**—Royal, 4.30.
Mathematical, 8.
Institute of Electrical Engineers, 8.
Royal Institution, 9. "The Three Stages of Shakespeare's Art," by Rev. Canon Ainger, M.A., LL.D.
- FRIDAY, 14th.**—Quekett Club, 8.
Astronomical, 3. (Anniversary).
Royal Institution, 9. "Problems in the Physics of an Electric Lamp," by Prof. J. A. Fleming, M.A., D.Sc.
- SATURDAY, 15th.**—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

A Gentleman (age 40) holding Advanced Science and Art Certificates in the following subjects wishes for appointment:—Mathematics (Second Stage); Sound, Light, and Heat; Electricity and Magnetism; Inorganic Chemistry; Organic Chemistry (Hon.); Geology; Human Physiology; Botany; Biology; Metallurgy; Steam and Applied Mechanics; National Medallist in Physiology; Trained in Chemistry, Physics, and Biology at Normal School of Science, London. Good Demonstrator and Lecturer.—Address, "Science," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1577.

ON THE GRAVIMETRIC COMPOSITION OF WATER.*

By W. DITTMAR.

ON the strength of Dumas's famous "Recherche sur la Composition de l'Eau" (*Ann. Chim. Phys.* (3), vol. viii., p. 189) all chemists, until lately, agreed in assigning to the atomic weight of oxygen the value $O = 16$ ($H = 1$); and it is on the strength, chiefly, of the same evidence that many of us now hold that $O = 15.96$ is a closer approximation to the truth.

In these circumstances it is surely worth while to look into Dumas's work with the help of critical experiments, and to try and see whether the great master was not right in thinking that, all his great efforts notwithstanding, the difference lies within the influence of his *method* errors, the more so as all these errors (as far as one can see without experimenting) tend to raise the experimentally ascertained value of the ratio $H : O$ above its true value.

I accordingly, some time ago, caused my private assistant, Mr. J. B. Henderson, to join me in this inquiry, and, thanks to his youthful energy and enthusiasm, we have already made considerable progress in our experiments, and hope, before long, to lay a complete account of them before the Society. Meanwhile, I content myself with stating that we have succeeded in so modifying Dumas's *modus operandi* as to give a higher degree of constancy to the weighings, and to reduce the trouble and loss of time involved to far less than it was with the original form of the method.

The principal object of the present communication, however, is to direct attention to an oversight which Dumas made himself guilty of, and which, as far as I am aware, has never been noticed before. What I allude to is that Dumas, while weighing his oxygen (virtually) *in vacuo*, weighs his water in air, and forgets to reduce this latter weight to the vacuum.

That the correction tells very appreciably on the calculated weight of the hydrogen, a very little reflection is sufficient to show; I prefer to at once give the results of my re-calculation of Dumas's results, and apply the correction to my "most probable" value.

In his tabular statement of results (p. 200 of his memoir) Dumas gives, in the case of each of his nineteen experiments, two values for what he calls the equivalent of hydrogen (the term meaning, with him, the weight of hydrogen which unites with 10,000 parts of oxygen into water), viz.: firstly, the value as calculated from the uncorrected weights of water and oxygen, and secondly, the "equivalent as corrected for the air in the sulphuric acid" (employed for the evolution of the hydrogen from zinc). For reasons which will be stated in our memoir I have left these corrected values on one side, and reduced only the "*equivalents bruts*."

Taking S as a symbol for the weight of oxygen consumed in a given synthesis, and W as representing the uncorrected weight of water produced, I formed the nineteen equations:—

$$\begin{aligned} W_1 - kS_1 &= \delta_1. \\ W_2 - kS_2 &= \delta_2. \\ W_3 - kS_3 &= \delta_3. \\ &\dots \dots \dots \end{aligned}$$

and solved these in respect of k , firstly, in the way which reduces the algebraic sum of all the errors δ to nil; and secondly, so as to reduce the sum of the squares of the errors δ to its minimum. The first method gave $k = 1.125, 43$; the second gave $k = 1.125, 47$. The two values, as we see, are almost identical. Adopting the second, it may be read as stating that 1000 grms. of oxygen take up hydrogen to form a quantity of water whose apparent weight in air is 1125.47 grms. But, assuming the air to have the density corresponding to 15°C. , and 760 m.m. (which probably is not far removed from the air density which actually prevailed during Dumas's work), the air displaced by the water amounts to 1.38 grms., whence we have, in reference to any given quantity of water, the following relative values for the weights of—

Oxygen.	Hydrogen.	Water.
1	0.126 85	1.126 85
8	1.014 8="H."	
15.767="O."	2="H ₂ ."	

The results of our own experiments tend to show that the true value of "H" ($O = 16$) is probably not quite so high as 1.0148, but it is higher than the 1.0024 demanded by the customary " $O = 15.96$."

I venture to hope that the publication of this notice will cause those chemists, who hitherto (after having become convinced that $O : H$ is less than 16) have persisted in referring their atomic weights to $H = 1$, will give up this absurd practice, and, as sensible people, adopt $O = 16$ as their standard. The sixteenth part of the atomic weight of oxygen, surely, is as good a unit as one could desire to have.

P.S.—The above had already been forwarded to the secretary of the Royal Society, when a friend directed my attention to a passage in Dumas's memoir, which I must confess had escaped my attention. In the course of his critical remarks on Berzelius's quantitative syntheses of water (by means of the oxide of copper method), Dumas points out that Berzelius ought to have reduced his water weights to the vacuum, but neglected this important correction.

With this sentence before one it is difficult to think that Dumas should have forgotten the very same correction in his own experiments, and yet I feel quite convinced he did, for the following reasons:—

1. While minutely describing his mode of weighing the oxide of copper, and the copper obtained therefrom in the same evacuated vessel, he is silent on this point in connection with the determination of the weight of water obtained.
2. Had he used the same method for the water which he adopted for the oxygen, the air-pump would have had to be attached to the last U-tube of the water apparatus, and, as at his time vulcanised indiarubber was not invented yet, we should see a stopcock at that U-tube in his very complete and detailed drawing of the apparatus. But no such thing is to be seen.
3. After having allowed his reduced copper to cool in hydrogen he detaches the bulb containing it, pumps out the hydrogen, and then weighs the evacuated apparatus. While this is being done a current of dry air is made to pass through the apparatus containing the water, to displace the hydrogen, and render the apparatus fit for the balance. If the water vessel was meant to be evacuated before being weighed, why not pump out the hydrogen?
4. Had Dumas weighed the water in the ordinary way, and then added on the weight of the displaced air, then, on the table of results (p. 200) the numbers given as representing the weights of water obtained could not agree with the differences between the weights of the water receptacle before and after the experiment.
5. Last, not least, the experiments made by Mr. Henderson and myself agree very nearly with Dumas's; and

* Read before the Royal Society of Edinburgh, February 3, 1890.

† As already pointed out by Lothar Meyer and Seubert, Dumas's table includes quite a number of misprints. These, however, are all easily spotted and set right without much fear of error.

they do so only as long as we neglect to correct our water weights for the displaced air.

ADDENDUM.—Not wishing to conceal anything that tends to invalidate my hypothesis, I will point out that Erdmann and Marchand, in their well-known syntheses of water, by means of the oxide of copper method (Erdmann's *Journ. f. Prakt. Chem.*, 1842, vol. xxvi., p. 461), obtained almost exactly the same value for H as Dumas did, although they did reduce their water-weights to the vacuum. But from their memoir it appears that, while they used (recently fused?) caustic potash for drying their hydrogen before it entered their oxide of copper tube, they dried the outgoing excess of hydrogen (and air at the end) only with (fused?) chloride of calcium. Now it is fair to assume that the caustic potash dried the gas completely, while we know, on the other hand, by Fresenius's experiments, that fused chloride of calcium leaves about one milligram of water in every litre of gas that enters the U-tube in a moist state. Hence, although Erdmann and Marchand, like Dumas, produced the correct amount of water from a given weight of oxygen, the German investigators had less water on the balance than Dumas, and came up to his number only by adding on the weight of the displaced air, which Dumas did not. As soon as we have completed our own experiments we shall try and see whether my premises are correct.

Anderson's College Buildings,
February 10, 1890.

ESTIMATION OF FATTY ACIDS IN ALIZARIN OIL.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

As one who has had a good deal of experience in the determination of fatty acids in oleine (alizerin or Turkey-red oil), perhaps I may be permitted to point out certain sources of error in the process proposed by Mr. Fred. Guthrie for this purpose (*CHEM. NEWS*, vol. lxi., p. 52). I think it only right to do this, because if Mr. Guthrie's process were generally adopted by chemists in calico printing and dye works, a serious injustice would be inflicted upon makers of and dealers in alizerin oil.

As ordinarily prepared, alizerin oil contains a small proportion of alkali combined with part of the fatty acids, the remainder of the fatty matter being present mainly in the form of free sulpho-fatty acids. In the case of oleine made from castor oil, the fatty matter consists largely of sulpho-ricinoleic acid, which, as everyone knows who has worked with this substance, is comparatively soluble in water.

The idea upon which Mr. Guthrie apparently bases his process is, that if alizerin oil be heated first with soda and then with a slight excess of sulphuric acid, the sulpho-compounds are decomposed, and may be removed by filtration and washing with boiling water. This idea is, I believe, quite erroneous. I am of opinion that if a fatty acid, e.g., sulpho-ricinoleic, be treated as described above, sulpho-ricinoleic acid would be again liberated. According to Mr. Guthrie, however, this is not the case, as he states that by working in the above-mentioned manner "the sulpho-fatty acids are decomposed, the sulphuric acid washed away; therefore the fatty acids do not blacken and decompose on drying at 212° F.," thereby implying that, in the case of oleine made from castor oil, ricinoleic, and not sulpho-ricinoleic, acid is the final product of his method of analysis. Even if this assumption were correct, the figures obtained by such a process would be totally unfair to the vendors of alizerin oil, and they would naturally decline to accept such results, for the simple reason that when they guarantee, say, 50 per cent fatty acids, they mean sulpho-fatty acids; whereas, if Mr. Guthrie's statement be accepted, his method would

indicate the percentage of ricinoleic acid—an altogether different thing.

One of the advantages which Mr. Guthrie claims for his process is that "the fatty acids are practically insoluble in boiling water." Now, I venture to say that this expression of opinion is contrary to the experience of all who have had occasion to work upon the fatty and sulpho-fatty acids of castor oil. Even ricinoleic acid is somewhat soluble in hot water, while sulpho-ricinoleic acid forms a white emulsion, some of which would certainly be carried away with the wash-water employed. It seems to me, therefore, that whether the result obtained be moderately near the truth, or decidedly too low, depends almost entirely upon the amount of washing to which the fatty acids are submitted.

The great objection to Mr. Guthrie's process is that he makes no attempt to substantiate its accuracy by comparison with other well known and reliable methods. Not a single figure is brought forward, nor the result of any experiment recorded, which might prove that the "threefold advantages" which the process is alleged to possess have any real foundation on fact.

It seemed worth while, therefore, to test the accuracy of the process on two samples of oleine, which I have just examined by my usual method. The results, which are given below, were, as I anticipated, much too low.

	Fatty acids, per cent.	
	Guthrie.	Williams.
No. 1 sample	38.4	46.9
No. 2 "	44.3	50.8

These figures are, I think, sufficient to convince anybody of the inaccuracy of the process which Mr. Guthrie recommends.

I may say, however, that the process failed still more signally when tried on a sample of 75 per cent oleine, such as is manufactured for export. The result was more than 12 per cent too low, the solubility of the fatty acids being very apparent in this particular case. There are one or two other points in the process to which exception might reasonably be taken, but I trust I have said enough to prove the unreliability of the proposed method.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
Feb. 4, 1890.

THE DETERMINATION OF SULPHURIC ACID IN PRESENCE OF IRON.

By G. LUNGE.

As far back as 1881 the author found that opening up iron pyrites in the wet way, for which he had proposed an especial method, did not give perfectly accurate results if the sulphuric acid is precipitated in the ferriferous solution. The precipitate always contains arsenic, and the results are rather too low (on an average, 0.18 per cent of sulphur in ordinary pyrites). The precipitate may, indeed, be obtained perfectly free from iron, but only by using great quantities of acid in washing, which dissolves away about 1 per cent of sulphur in the state of barium sulphate. This may, indeed, be recovered, but it is better, before precipitating the barium sulphate, to throw down the ferric oxide by means of a moderate excess of ammonia, and to wash upon the filter with boiling water. Even with a single precipitation it is quite possible to render the precipitated ferric oxide perfectly free from sulphur, which was ascertained by drying the precipitate, fusing with soda, and testing the solution for sulphuric acid, of which not even a trace was ever found.

This method, after its description in the "Pocket-Book for the Alkali-Manufacturer" (1883), was brought into very general use both in Germany and England for the valuation of iron-pyrites.

Though the experiments of Jannasch and Richards did not relate to this latter improved method, but to the author's former one (which he had himself pronounced not perfectly accurate), the suspicion might arise among the many chemists interested whether the more recent method (of 1881) was in question. To remove this doubt and to satisfy himself that no error had occurred in his experiments, he caused the question to be independently re-examined by Herrn Barbezat and Obregia.

H. Barbezat showed that the precipitation of the ferric hydroxide must be effected exactly as laid down by the author in 1881, *i.e.*, the moderately warm liquid must be mixed with ammonia in moderate excess, let stand for about ten minutes, then filtered and washed upon the filter with boiling water, keeping the precipitate constantly stirred up. In this case the ferric hydroxide retains no sulphur. But if the operator proceeds—as it is elsewhere directed for the precipitation of the iron—by adding a very slight excess of ammonia and removing this by prolonged boiling, there remains behind a very appreciable quantity of basic ferric sulphate, up to 3.6 per cent of the total sulphur. Hence this method should not be adopted.

H. Obregia made direct comparative experiments on very pure Spanish pyrites, in which there was no reason to fear any complication in the comparison of the methods from the presence of galena, &c. He determined the sulphur according to the three following methods:—A, by opening up with a mixture of 1 part hydrochloric acid, 3 parts nitric acid, and direct precipitation with barium chloride (*i.e.*, according to Prof. Lunge's earlier method, which he had pronounced not perfectly accurate as far back as 1881); B, opening up as above, precipitating and washing the ferric hydroxide, and afterwards precipitating with barium chloride (*i.e.*, Prof. Lunge's method of 1881). Here he generally succeeded when operating upon 1 grm. pyrites to obtain not more than 200–250 c.c. of liquid *before* adding the barium chloride, so that the precipitation of the sulphuric acid could be effected at once without concentration. C, by opening up with soda, exactly according to the method of Fresenius employed by Jannasch and Richards.

In the series of experiments, B, the iron precipitate was also fused with soda and tested for sulphuric acid, not a trace of which was ever found, exactly as in the experiments of Prof. Lunge in 1881.

The following are the proportions of sulphur found:—

A. Lunge's old method.	B. Lunge's method of 1881.	C. Method of Fresenius.
52.38	52.70	52.46
52.38	52.41	52.49
51.94	52.22	52.31
	52.26	
	52.39	
Mean.. 52.23	52.40	52.40

Hence the following conclusions may be safely drawn:—

1. The author's method of 1881, above described, gives results which quite agree with those of the saltpetre-soda melting process of Fresenius. If we reject the first of the experiments B as probably too high, the mean of the series is 52.32, *i.e.*, only 0.1 per cent lower than the mean of the Series C.

2. It is fully proved that the iron precipitate, if properly treated, retains no sulphuric acid.

3. The former opinion of Jannasch and Richards, that the Lunge process, from a purely scientific view, must be rejected, is not applicable to the process described in 1881. This is found quite as accurate as that of Fresenius, and has the advantage of requiring less time and less skill, and of not ruining platinum crucibles. In the rare cases when it is requisite to determine the sulphur present in

heavy spar and galena, this can be effected by fusing the residue insoluble in acids with soda.—*Journal für Praktische Chemie.*

ON THE DECOMPOSITION OF ORGANIC MATTER IN WATER.*

By MARK POWERS.

THE experiments herein detailed were undertaken with a view to obtain more exact information in regard to the decomposition of organic matter in water. While we have experimental evidence bearing on many points in connection with the subject, a review of this evidence will show that in many cases conclusions have been drawn which can be scarcely justified by the facts already known. We find many conflicting statements in the literature of the subject, and because of this fact and of the undoubted importance of the question, I have thought it worth while to repeat certain experiments with such modifications as would be most likely to reveal the truth in each instance. I have also endeavoured to obtain further facts to aid in the solution of the problem.

The organic matter dissolved by water or held in suspension is derived from the decay of the proximate constituents of plants and animals, and may be taken up at any stage of this process. The compounds which enter into the composition of this matter are more or less unstable, undergoing change with ease, and very little is known concerning their individual properties. The element of danger does not arise from any inherent toxic properties of these compounds, but from the fact that water containing such matter serves as an excellent means for the development and distribution of disease germs. Certain products of decay are much more harmful than others in this respect, and certain conditions lend special power to bring about harmful results.

Simple oxidation, putrefaction, and the different varieties of fermentation are the chief agencies which effect this decomposition. Carbon dioxide, water, and ammonia are the principal ultimate decomposition products of organic matter. Ammonia may undergo the further transformation into nitric acid. The intermediate products are quite numerous and complex. Carbohydrates yield by fermentation a large number of alcohols, aldehydes, ethers, and acids of the fatty series. Vegetable matter in contact with moist soil is converted into a brownish black mass or humus which contains a great many unstable organic compounds. The fat yields glycerin and fatty acids. Fæcal matter contains undigested food and numerous decomposition products of albuminous matter and other proximate constituents of food. The albumenoids, including egg albumen, casein, blood-fibrin, peptones, &c., and the closely related bodies, such as gelatin and chondrin, yield a large and very important class of compounds. The principal products are the amido-derivatives of the fatty acid series—leucine, glycocoll, aspartic and glutamic acids, &c., members of the fatty acid series—formic, acetic, propionic, butyric, &c., the compound ammonias—methylamine, ethylamine, propylamine, &c., members of the aromatic group—phenol, cresol, skatol, indol, tyrosin, hydroparacumaric acid, alphaltoluic acid, &c. These compounds yield simpler products by further decomposition. Albuminous matter enters largely into the composition of the animal body, and is found in small quantity in nearly all parts of the plant, with the exception of the seed, where it occurs more abundantly. It is the decomposition of these highly complex nitrogenous compounds in water that introduces the element of danger, as the organic nitrogen results almost entirely from the decomposition of albuminous

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matter and derived products. The amount of free ammonia and nitric acid indicates with more or less accuracy the extent of changes which have already taken place. In the following experiments an attempt has been made to furnish data from which more accurate conclusions may be drawn concerning the organic matter in water by the study of individual deportment in case of the principal constituents of this matter. Each compound, when subjected to the tests, decomposes in a manner peculiar to itself.

Total Conversion of the Nitrogen of Albumen into the Form of Ammonia.

Wanklyn's statements upon this subject are rather indefinite. This author mentions experiments of his own by which almost all of the nitrogen of albumen is converted into the form of ammonia, but does not give the details of his work. He was at first inclined to believe that the ammonia obtained was a definite portion of the total amount. According to other chemists, only a fraction of the total nitrogen of albumen will yield ammonia when boiled with permanganate solution. The details of my own experiments are given for the purpose of showing under what circumstances the total nitrogen of albumen is evolved in the form of ammonia.

Fresh White of Egg Solution No. 1.—Containing 30 grms. of fresh white of egg dissolved in 2500 c.c. water. 10 c.c. of this solution were diluted to 500 c.c., 5 c.c. of a strong solution of Na_2CO_3 , free from ammonia, were added, and the mixture distilled. Four distillates of 50 c.c. each were removed for the estimation of "free ammonia," then 50 c.c. of a solution containing 8 grms. potassium permanganate and 200 grms. potassium hydrate per litre were added, and four more distillates of 50 c.c. each were nesslerised for the "albumenoid ammonia." By continued boiling of the same portion of this solution with permanganate mixture on successive days, the total nitrogen in egg albumen appears in the form of ammonia. Before each distillation 200 c.c. of pure water was added to the contents of the retort. The retort was kept tightly stoppered during intervals between successive distillations in order to preserve the solution free from atmospheric impurities. Care was taken to wash the condenser thoroughly with water free from ammonia before being used. An aliquot part of the first distillate was taken for comparison with standards where depth of colour would interfere with accuracy.

In calculating the amount of ammonia which by theory should be obtained from a certain weight of white of egg, I have taken the values usually given (see König's "Nahrungsmittel"), viz., 12.5 per cent of albumen with 15.7 per cent of nitrogen. Under theory, the values so obtained are given below.

	Free Ammonia. M.grm. NH_3 .	Albumenoid Ammonia. M.grm. NH_3 .
First distillation ..	0.0675	1.420
Second ..	0.270	0.270
Third ..	0.146	0.146
Fourth ..	0.095	0.095
Fifth ..	0.061	0.061
Sixth ..	0.037	0.037
Total amount ..	2.029	
Theory ..	2.85	

Solution of Egg Albumen No. 2.—Containing 48.710 grms. fresh white of egg dissolved in 2500 c.c. water. 10 c.c. of this solution were taken for distillation. The same precautions as given above were taken with this series of distillations. (See next column).

Egg Solution No. 3, made by dissolving dried albumen in distilled water, was decomposed much more slowly.

It will therefore be observed that it is possible, by continued distillations with alkali-permanganate solution to convert the total nitrogen of albumen into the form of ammonia. Egg solution No. 2 yields nearly 95 per cent

	Albumenoid Ammonia. M.grms. NH_3 .
First distillation ..	2.620
Second ..	0.475
Third ..	0.210
Fourth ..	0.208
Fifth ..	0.153
Sixth ..	0.122
Seventh ..	0.095
Eighth ..	0.099
Ninth ..	0.075
Tenth ..	0.070
Eleventh ..	0.060
Twelfth ..	0.050
Thirteenth ..	0.038
Total amount ..	4.275
Theory ..	4.63

of this element. The decomposition is, however, very slow under the conditions of the experiment. The rate depends upon a variety of circumstances—the concentration and quantity of permanganate solution, shape and size of retort, rapidity of distillation, &c. In egg solution No. 1 about 50 per cent of the nitrogen in the form of ammonia was evolved during the first distillation; in solution No. 2 a larger proportion, while from a solution of dry albumen in water only a little over 35 per cent of the total amount was obtained.

Decomposing Solution of Egg Albumen.

Fresh white of egg solution No. 1 was allowed to putrefy, and the process of decomposition was traced from the beginning by means of the amount of free and albumenoid ammonia evolved. 10 c.c. were taken for each test. Precautions were taken to keep the room as free as possible from ammonia vapour or other substances liable to contaminate the solution. I am not aware that anyone has traced the process of decomposition of albumenoid material in this way. The conditions simulate those that exist in natural waters. Tiemann and Preusse have traced the process of decomposition of egg albumen by means of the oxidation test with standard solution of potassium permanganate, but only for a short time.

	Free Am. m.grms. NH_3 .	Alb. Am. m.grms. NH_3 .
Feb. 19..	0.072	1.420
" 26..	0.067	1.120
Mar. 5..	0.110	1.113
" 12..	0.442	1.068
" 19..	0.623	1.055
" 26..	0.890	1.015
April 2..	0.940	0.958
" 9..	0.978	0.838
" 16..	1.013	0.763
" 23..	1.327	0.700
" 30..	1.375	0.680
May 7..	1.525	0.595
" 14..	1.635	0.578
" 21..	1.680	0.541
" 28..	1.785	0.496
June 4..	1.904	0.455
" 11..	1.965	0.444
" 18..	2.035	0.413
" 25..	2.206	0.352
July 2..	2.127	0.355
" 9..	2.129	0.304
" 16..	2.140	0.298
" 23..	1.990	0.320
" 31..	2.092	0.320
Aug. 13..	1.915	0.322
" 27..	2.124	0.332

Putrefying solution of egg albumen yields a gradually increasing quantity of free ammonia, while the albumenoid ammonia regularly diminishes. The free ammonia plus

the albumenoid ammonia is an increasing quantity, and near the latter part of the time occupied by experiment is above 90 per cent of the total nitrogen.

Urea.

There are, perhaps, more conflicting statements in regard to the decomposition of this compound than any other. Wanklyn states that urea, when quite pure, may be boiled for a long time with alkalis without evolving a trace of ammonia, and again, in presence of permanganate and excess of potash, urea is doubtless decomposed, but it yields no ammonia. Tiemann obtains, on the other hand, the total nitrogen in the form of ammonia. Other chemists assert the possibility of obtaining the total amount. In one of Wanklyn's experiments, by boiling for a long time with strong permanganate mixture, only 22 per cent could be obtained. The details of my own experiments with this compound are given below.

The total nitrogen of urea is converted into ammonia if a simple solution in water is boiled during a sufficient length of time. The decomposition is more rapid if strong solution of alkali permanganate be added.

Experiment 1.—2.5 m.grms. urea were dissolved in 500 c.c. water, and 5 c.c. of a strong solution of Na_2CO_3 added, and the mixture distilled for free ammonia, after which 50 c.c. of permanganate solution were added for the albumenoid ammonia.

Free ammonia = $0.028 + 0.014 + 0.012 + 0.011$ m.grm.
 $\text{NH}_3 = 4.5$ per cent NH_3 .

Albumenoid ammonia = $0.033 + 0.022 + 0.021 + 0.027 + 0.056$ m.grm. $\text{NH}_3 = 11$ per cent NH_3 .

Total = 15.5 per cent of theoretical yield of NH_3 .

Experiment 2.— $\frac{1}{2}$ m.grm. urea—otherwise same as in Experiment 1.

Free ammonia = $0.022 + 0.012 + 0.0015 + 0.001$ m.grm.
 $\text{NH}_3 = 12$ per cent NH_3 .

Albumenoid ammonia = $0.022 + 0.007 + 0.005 + 0.003$ m.grm. $\text{NH}_3 = 13$ per cent NH_3 .

Total = 25 per cent of theoretical yield of NH_3 .

Experiment 3.— $\frac{1}{4}$ m.grm. urea—100 c.c. permanganate solution.

Free ammonia = $0.022 + 0.012 + 0.0015 + 0.0015$ m.grm.
 $\text{NH}_3 = 13$ per cent NH_3 .

Albumenoid ammonia = $0.020 + 0.012 + 0.012 + 0.0125$ m.grm. $\text{NH}_3 = 19$ per cent NH_3 .

Total = 32 per cent of theoretical yield of NH_3 .

Experiment 4.—1 m.grm. urea—2 grms. potassium permanganate and 40 grms. potassium hydrate added for albumenoid ammonia.

Free ammonia = $0.034 + 0.025 + 0.012 + 0.0075 + 0.005$ m.grm. $\text{NH}_3 = 16$ per cent NH_3 .

Albumenoid ammonia = $0.068 + 0.023 + 0.021 + 0.0225 + 0.030$ m.grm. = 28 per cent NH_3 .

Total = 44 per cent of theoretical yield of NH_3 .

Experiment 5.—1 m.grm. urea in 450 c.c. water with 50 c.c. permanganate solution added. Boiled during ten hours in retort with inverted condenser and bulbs containing dilute solution of sulphuric acid attached at other end. Two sets of bulbs were employed and blank experiments were made in order to test the connections of the apparatus, and to ascertain if any other sources of error might be present in the experiment. The amount of ammonia obtained in the blank trial was so small as to be neglected altogether. The albumenoid ammonia obtained from urea was 78 per cent of the total amount. By distilling off four distillates of 50 c.c. each for four successive times, the remaining 22 per cent of the ammonia was obtained.

Experiment 6.—2 m.grms. urea. Boiled solution during twenty hours—otherwise same as in Experiment 5. Albumenoid ammonia obtained, 101 per cent.

Experiment 7.—2 m.grms. urea. Boiled during twenty-two hours in 500 c.c. water only. Ammonia obtained, 95 per cent of the theoretical amount.

In this connection the results obtained by Dr. Charles Smart are of interest (*Sanitarian*, Nov., 1886). He states:—"Since 1 m.grm. urea in 500 c.c. of water gives a persisting and equable evolution of 0.01 m.grm. of ammonia when distilled alone or with sodium carbonate, and an evolution of 0.02 in each measure when subsequently treated with alkaline permanganate, a water sample which yields such results must have contained urine equivalent to, at least, 1 m.grm. of urea," and again, "a water which yielded in successive distillates of 50 c.c. each 0.47, 0.25, 0.15, and 0.15 m.grm. of free ammonia, and afterward, 0.54, 0.34, 0.32 and 0.32 m.grm. of albumenoid ammonia, might be set down as having contained urine equivalent to, at least, 15 m.grms. of urea in the 500 c.c. of water used in the experiment." If these statements expressed the real facts in the case the observation would doubtless be of great value. The equable evolution refers to the third, fourth, and subsequent distillates, and the results are in direct proportion to the amount of urea present. The experiments I have made with urea prove that no set or combination of conditions can concur to produce such an evolution of ammonia. The decomposition of urea takes place very slowly, even with strong solution of permanganate, but wide variations result from apparently slight changes in the conditions of the experiment. My experiments were made in as nearly uniform a manner as possible, with reference to the time in collecting distillates. Experiments 2 and 3, with one-fifth as much urea as in Experiment 1, gave, on the other hand, nearly twice the quantity of total ammonia, and furthermore, a comparison of the third, fourth, and subsequent distillates in each case reveals the fact that the amount of albumenoid ammonia evolved is from two to six times the quantity of free ammonia, and is not in the constant ratio of 2:1. The evolution of ammonia from urea is quite variable, and being associated in natural waters with other nitrogenous compounds of unknown character, there is no trustworthy evidence that will determine the quantity of the substance with the degree of precision stated by this author.

(To be continued).

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

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(Continued from p. 72).

General Results of former Determinations most deserving Confidence.

THESE recent researches, unquestionably by far the most valuable up to the present time, give us, when taken separately and together, the following values for the atomic weight of gold:—

1. General mean of 5 series by Krüss, as calculated by himself 196.640
2. General mean of 3 series by Thorpe and Laurie, as calculated by themselves 196.852
3. 1 and 2, giving equal value to each 196.746

Difficulties to be overcome in Determining the Atomic Weight of Gold.

Besides the special difficulties connected with each method which may be adopted, the determination of any high atomic weight with a degree of accuracy which enables the result to be accepted to a given decimal place is clearly a much less easy matter than would be the

* A Paper read before the Royal Society, May 9, 1889.

attainment of an apparently equal degree of precision for an atomic weight represented by a small number. In obtaining the atomic weight of lithium, the first with which, many years ago, I had any personal experience, a difference of unity in the first decimal place corresponded to about $\frac{1}{10}$ th of the whole value considered to be correct. In getting the atomic weight of aluminum, worked on later, a like difference represented approximately $\frac{1}{10}$ th of the whole value. But, in the case now considered, of the atomic weight of gold, unity in the first decimal place means but about $\frac{1}{10}$ th of the whole value. So that, looking at the matter in this light, it may be said that a degree of precision is demanded more than seven times as great as in the case of aluminum, and twenty-eight times as great as in the case of lithium.

There is also to be noticed, as the most obvious *general* difficulty to which all methods for determining the atomic weight of gold are more or less exposed, the instability of compounds of this metal; not merely the ease with which complete decomposition occurs, with separation of free gold, but the much more insidious and less easily detected trouble arising from the comparative ease with which aurous pass into auric compounds, and the reverse.

New Experiments by the Author.

The general difficulties just alluded to, and the special points to be investigated in regard to each method of determination tried, have demanded much time and work, and I cannot feel even now that all has been done that is desirable and possible; but the experiments projected have been so far completed as to seem to justify publication, and I am not likely soon to be able materially to extend them.

General Principles kept in View.

The improvements made of late years in manipulative methods and apparatus have tended to reduce very much the magnitude of what are commonly called "fortuitous" errors in our quantitative determinations of matter, and to increase greatly the accuracy of such determinations. Probably no modern work has had more influence in this direction than the classic researches of Stas on certain atomic weights—the precautions taken by him, and his remarkable manipulative skill, causing his results to bear almost the same relation to those of his immediate predecessors as did those of Berzelius to the work of the chemists of his earlier day. No one nowadays would undertake the determination of the atomic weight of one of the better known elements without taking such elaborate precautions as practically ensure pretty close concordance of results, when obtained by the same method, applied in the same hands. In the present state of the question of atomic weights and improvement in their determination, advances in mere delicacy of manipulation and success in merely securing close agreement of results by the same method are not alone sufficient. It cannot be too much insisted upon that we need, besides, well-directed and laborious investigation of possible sources of *constant errors*, and the adoption of means to guard against them. Careful preliminary study is required, in a general way, of the precise nature of each reaction employed, and how it may be influenced by the conditions of the experiment. We learn more and more of late that many of the reactions—perhaps it should rather be said all of the reactions—which have been generally supposed to be of the simplest nature are in reality complex.

The following are among the general principles which seem to be most important, as tending to greater accuracy and trustworthiness in atomic weight determinations; they have been in part stated in the author's earlier paper on the atomic weight of aluminum:—

1. In purifying the materials used, both the element of which the atomic weight is to be investigated (or any special compound containing it) and all substances used to react thereupon, resort should in all cases be had to

"fractional" methods, assuming materials to be pure only when earlier and later fractions give no signs of any constant difference in the results which they yield.

2. Different and independent processes should be applied to the determination of the same atomic weight, and the results used to check each other. It is desirable that as many such different processes be applied as can be devised, provided each be reasonably free from apparent sources of error, even though it be usually impossible to properly assume that all are equally advantageous in this respect, and therefore of equal value. In the comparison of results obtained it should be noticed whether a given method tends on the whole to yield results probably higher or lower than the truth, though it may be gravely doubted whether the practice is commendable of attempting any numerical estimate of relative value, by so-called "weighting" of the results in calculation.

3. In connection with each process there should be careful study of the reactions depended upon for the final determination of an atomic weight, looking especially to the possibility of the occurrence of secondary or subsidiary reactions.

4. Each process adopted should be as simple as possible, both in the nature of the chemical reaction or reactions, and in the known liability to merely manipulative errors.

5. Each process should be carried out with, in some experiments larger, and others smaller, quantities of material. But, on the whole, the quantities used should be kept within such limits as are most likely to admit of most accurate determinations being had under the conditions of the special process.

6. In the reactions depended upon, only such other elements should be concerned as may be counted among those of which the atomic weights are already known with the nearest approach to exactness.

7. It is particularly desirable that, if possible, the atomic weight to be investigated shall be, by at least one process, compared directly with that of hydrogen, now almost universally taken as the basis for the whole list of the elements. It is remarkable for how very few of the elementary substances—not more than three or four—this direct comparison has been accurately made.

8. In the greater number of the processes available for atomic weight determinations the comparison with hydrogen must perforce be made indirectly. When this is the case, it is desirable that as few other elements as possible the assumed atomic weights of which will have to be taken into account shall be involved in each single reaction depended upon.

9. In selecting *different* processes to be applied to the determination of the atomic weight of a given element, in order that the results may check each other, it is desirable that, not the same, but as many different other elements as possible, shall be concerned in the several reactions, provided all such elements count amongst those of which the atomic weights may be considered in the first rank as to the accuracy with which they are known.

Means and Methods of Weighing Employed.

These were in the main the same as those which I had in former years used in determining the atomic weight of aluminum.

The balance chiefly used, made by Becker, was carefully cleaned, and all its parts adjusted, especially as to the position of the centre of gravity for each load to be used. A second balance, by the same maker, of larger size, capable of taking a load of a kilogram, in each pan, was employed in weighing certain of the solutions experimented on, and was in like manner carefully adjusted and tested. All weighings were made by observation of the oscillations of the index on either side of the position of rest. A difference of weight of 0.0001 grm. with the smaller balance, and 0.0002 grm. with the

larger instrument, was easily and distinctly observable with any load which the research required.

The same kilogram. weight was made the basis of a comparison with all my other weights which had been before used in the same way. This had been compared at Washington with the "star kilogram." of the United States Coast Survey, the value of which is known in terms of the original "kilogram. of the Archives" at Paris. All the smaller weights were carefully re-checked against this and against each other, and their real values ascertained as referred to a vacuum. The necessary determinations were made of the specific gravity of all materials and vessels which were to be weighed, and the barometer and thermometer were read at the time of each weighing, so that all weights recorded in this paper represent real values *in vacuo*. In order to reduce to a minimum errors due to varying deposition of hygroscopic moisture, vessels of like material, shape, and size with those used to contain substances to be weighed were used as tare.

History and Mode of Purification of the Gold used in this Research.

Most of the metal needed was prepared by myself, with precautions presently to be mentioned; a part was obtained as "proof gold," from the United States Mint at Philadelphia; another part from the United States Assay Office at New York; and a single specimen of English "trial plate" gold from the Royal Mint in London.

1. *Purification of Gold by the Author.*—It may fairly be concluded from the general history of the gold of commerce, that the impurities most to be suspected, and most requiring special precautions for their removal, are silver and the metals of the platinum group. My preliminary experiments led me to believe that the greatest difficulty in the way of obtaining perfectly pure gold consists in getting rid of the last traces of silver, the chloride of this metal not being quite insoluble in a solution of auric chloride. For the removal of silver, I have chiefly depended upon evaporation of the gold solution with a little hydrobromic acid, followed by large dilution with water, and long-continued clearing by subsidence. As regards the platinum metals, my results agreed substantially with those of Hoffmann and Krüss,* but I have been inclined to lay some stress on reduction of the gold from its solution with exclusion of light, and on fractional reduction, using only the middle portion thrown down. I avoided altogether the use of ferrous salts as reducing agents, in view of the difficulty of preparing them in large quantity with assurance of their purity, and the trouble of thoroughly washing the precipitated gold. For the final precipitation of the gold, formic acid seemed to offer real advantages; its volatility admits of easily getting it free from any metallic contamination, and the reduction is more easily effected than with oxalic acid.

Starting with United States gold coin, it was first heated to bright redness in a muffle, as a precaution against the presence of any traces of mercury, and to remove any grease, &c., from the surface, and then dissolved in a mixture of pure hydrochloric and nitric acids in the right proportions. The solution was evaporated with excess of hydrochloric acid nearly to dryness, the auric chloride re-dissolved in a considerable quantity of water, and the solution allowed to settle for four or five days. The greater part of the clear liquid, drawn off with a syphon, and filtered through very siliceous sand,† was again evaporated nearly to dryness, adding towards the end a few drops of pure sulphuric acid, in case of the conceivable, though unlikely, presence of such traces of lead as this might reveal; much pure water was added, the

solution again cleared by subsidence for several days, and the greater part of the clear liquid again drawn off and filtered. This solution was now rendered pretty strongly acid with hydrochloric acid, and fractionally precipitated by sulphurous acid (SO_2 was evolved from sodium sulphite), at as low a temperature as possible, and in the dark, putting aside the first and last portions of the metal thrown down, and reserving for further treatment the (largest) middle portion. The gold thus obtained was well washed with water, boiled with nitric acid alone, again washed, boiled with hydrochloric acid alone, again washed, dried, and heated strongly with fused acid sulphate of potassium in a porcelain crucible, boiled with dilute hydrochloric acid, and then with water. The metal was re-dissolved in aqua regia, the solution evaporated nearly to dryness, with addition of pure hydrobromic acid towards the end, very largely diluted with water, and allowed to stand for two days, well protected from dust, before again syphoning off as much of the clear portion as could be safely removed without risk of disturbing the remainder at the bottom, using a conical precipitating jar with greatest diameter below, and filtering the liquid through siliceous sand as before. The evaporation with hydrobromic acid was repeated twice more, and the clear solution—allowed the last time to stand a month before being syphoned off and filtered—was then reduced, once with oxalic acid (neutralising the liquid with pure sodium hydroxide from the metal), once (after re-solution) with sulphurous acid, and once with formic acid, washing the reduced metal well each time before re-dissolving in aqua regia. In the first and second of these reductions a little of the metal first and last thrown down was rejected, and in the final reduction with formic acid the first portion precipitated, about one-fifth of the whole, was reserved for use, labelled A, a, the middle portion, about three-fifths, was labelled A, b, and the last portion, the remaining one-fifth, was also preserved for use, marked A, c, so that it might be seen whether any difference in the character of the metal could be detected in the atomic weight determinations. All of these fractions received a very thorough final washing with water.

Such part of the purified metal as was to be used in the preparation of gold compounds was not fused, but was heated in a glazed porcelain tube to a moderate redness in a Sprengel vacuum. A small part of the metal used in the free state, and desired in compact form, was fused in a perfectly clean Beaufaye crucible with a little acid sulphate of potassium and borax, the button flattened, boiled with strong nitric and then strong hydrochloric acid, thoroughly washed with water, and, finally, heated in the Sprengel vacuum. Throughout the long process of purification, and especially towards its close, the most scrupulous care was taken to exclude dust, and to prevent grains of sand from the bottoms of beakers or any other impurities getting into the precipitated gold, upon which the acids used would not act, so as to obviate the risk of merely mechanical contamination, which, if overlooked, might lead to that being weighed as part of the gold which was, in fact, foreign to it.

2. *Purification of "Proof Gold" obtained from the United States Mint at Philadelphia.*—I owed to the kindness of Mr. J. B. Eckfeldt, Chief Assayer to the Philadelphia Mint, a liberal supply of the "proof gold" used in checking the gold assays there made, and he furnished me the following statement of the manner in which this purest metal is prepared, under his directions:—"The best cornets from the gold assays selected and dissolved in aqua regia. Solution evaporated, with additions of HCl , to nearly crystallisation, diluted largely with water, and allowed to stand for three or four weeks. About seven-eighths of the solution drawn off from the silver chloride, and passed through several thicknesses of various filters. Solution somewhat concentrated, and alcohol and potassium chloride added, allowed to stand

* *Liebig's Annalen*, vol. cccxxviii., p. 66.

† The sand was carefully purified beforehand by boiling with nitric and hydrochloric acid, thorough washing with water, and heating to redness in the air.

for some time (precip. traces of platinum*), and carefully filtered. Gold precipitated by addition of pure ferrous sulphate. Reduced gold washed repeatedly in boiling HCl, until washings show no iron, then well washed in pure water. Gold dissolved, and solution evaporated to crystallisation, with repeated additions of hydrobromic acid,† diluted, and again allowed to stand for some time; filtered. Through the solution was passed pure SO₂ until all the gold was reduced; washed. Gold again dissolved, evaporated with HCl, diluted, and oxalic acid added, and heated until all gold is down, melted in white clay crucible with potassium chlorate and nitrate, afterwards with pure sodium carbonate and borax." Mr. Eckfeldt also informed me verbally that the proof gold thus purified is cast into a small bar in a perfectly clean and bright cast-iron mould; the bar is boiled in nitric acid, washed, and dried, rolled between fine steel rolls quite free from grease, and the strip finally cleaned for use with hot hydrochloric and then nitric acid.

In a letter of later date he wrote:—"In preparing the 'proof' I seldom make over 10 ozs. in one lot; from 8 to 10 ozs. is the usual amount. There is comparatively little trouble in making 999.9 fine, but beyond that it is rather troublesome; and it seems that, with all the care, the final result is sometimes a little in doubt."

The fine gold received from the Philadelphia Mint is designated as B in this paper, in connection with the experiments in which it was used.

3. *Purification of "Proof Gold" obtained from the United States Assay Office at New York.*—Dr. H. G. Torrey, Chief Assayer in this Office, was obliging enough to let me have several samples of his finest proof gold, used in checking the regular assays in his department. He informed me that this proof gold was independently prepared at New York, but was occasionally compared with that of the Philadelphia Mint. He furnished the following brief statement as to its preparation:—"The process used in preparing the gold is to dissolve 'cornets' (or gold from assays) in nitro-hydrochloric acid, and after filtration precipitating by oxalic acid, and after thorough washing, melting under borax. The operation is conducted with the utmost care throughout."

The gold from this source is designated as C in this paper.

4. *Gold from the "Trial Plate" of Fine Gold of the English Mint.*—Professor Roberts-Austen, Chemist to the Royal Mint, was so kind as to let me have a specimen of a few grms. of gold cut from the trial plate of the pure metal prepared by him in 1873. In its preparation use was made of potassium chloride and alcohol to separate any platinum present in the original material, a long period of subsidence was allowed for the deposit of any silver chloride from the solution, and the whole process was applied on a large scale, resulting in the purification of some 70 ozs. of fine gold, of which Professor Roberts-Austen himself has said:—"I have not been able to prepare, or to obtain from any source, gold of greater purity, even in small quantities." It seems, however, that the apparent standard of this gold was slightly reduced in rolling, the finished plate being counted as 999.95 fine in comparison with the same gold before rolling. A memorandum given me by Professor Roberts-Austen states that this trial plate gold is 999.98 fine as compared with the purest gold obtained by Stas for the Belgian Mint.

This specimen of English trial plate gold is designated as D in the present paper.

All the samples of gold received from others—B, C, and D—were, before using them, carefully boiled in nitric

acid to remove any possible traces of silver or other metal derived from the shears used in cutting the plates. They were also previously well washed with ether, to remove any grease, and afterwards with pure water, and were finally heated to redness in the Sprengel vacuum.

It may be remarked, in advance, that I have not been able to trace any probable connection between the history of the several samples of gold used and the values obtained for the atomic weight of the metal. Within the limits of accuracy attained, the results appear to have been sensibly the same by each method for all the gold used. Nor is there apparent in the results of Kriess, or those of Thorpe and Laurie, any evidence of a difference fairly traceable to the nature of the metal employed by them.

A considerable part of the gold prepared by myself was, after having once served for a determination of the atomic weight, re-dissolved and re-precipitated, and was afterwards more than once used in subsequent determinations, and yet no sign was obtained of any resulting influence upon the later values of the atomic weight as obtained, evidence being thus furnished of the purity, not only of the gold itself, but of the reagents used to act upon it, so far as any contamination of the metal was concerned. It may, therefore, be concluded with reason that the gold used in these experiments was of uniform character, and uniformly free from any known impurities, to such an extent, at any rate, as to sensibly change the results obtained.

It is to be noted that the only known elements having higher atomic weights than that of gold are mercury, thallium, lead, bismuth, thorium, and uranium. The presence of any of these in the gold experimented on, even in traces too minute to weigh, is in a very high degree unlikely. The presence of any other element or elements than these would, for analogous compounds, tend to lower the value obtained for the atomic weight of gold; so that, in considering the chances of error due to the nature of the metal used as gold, we should be inclined to say that the risk was rather in the direction of too low than too high a result being reached. But, if the possibility be observed of compounds not analogous being erroneously compared, the contrary error will be seen to be possible. Thus, in case the composition of an auric haloid salt obtained from a given amount of metallic gold should be examined, if any unsuspected silver were present there would be required for the same amount of the halogen three atoms of silver instead of one atom of gold, and, therefore, the apparent weight of gold as compared with that of the halogen would be increased instead of diminished, and a higher value obtained for the atomic weight sought.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 7th, 1890.

Prof. REINOLD, F.R.S., President, in the chair.

The Reports of the Council and of the Treasurer were read and adopted. The former stated that there had been a very satisfactory increase in the number of members during the year. The number now exceeds 360, of whom 80 are Fellows of the Royal Society.

During the year the Council had proposed to change the time of meeting of the Society from Saturday afternoon to Friday evening. The change was adopted by the members by a vote of 129 to 30, and had resulted in a larger attendance at the meetings.

During the year the second part of Volume I. of the translations of important foreign memoirs had been issued

* The platinum of South American native gold, and of scrap gold from dentists, is at the Philadelphia Mint separated solely by alloying with enough silver, and dissolving out the latter metal with nitric acid. The platinum dissolves with the silver.

† I had, many months before, independently adopted and used hydrobromic acid to remove traces of silver more effectually than by hydrochloric acid, when I learned from Mr. Eckfeldt that he had thus habitually employed it.

to the members, and it was hoped that a third part would be published early in the present session.

The Council had to regret the loss by death of three well-known members—James P. Joule, Warren de la Rue, and Father Perry.

A valuable collection of books had been given the Society by the Royal Astronomical Society.

From the Treasurer's Report it appeared that the balance of the Society had been increased by £120 during the year.

Prof. Hittorf, of Münster, was, at the recommendation of the Council, elected an Honorary Member of the Society.

The result of the new election of officers was declared as follows:—

President.—Prof. W. E. Ayrton, F.R.S.

Vice-Presidents.—Dr. E. Atkinson, Walter Baily, M.A., Shelford Bidwell, F.R.S., and Prof. S. P. Thompson, D.Sc.

Secretaries.—Prof. J. Perry and T. H. Blakesley, M.A., M.Inst.C.E.

Treasurer.—Prof. A. W. Rücker, F.R.S.

Demonstrator.—C. V. Boys, F.R.S.

Other Members of Council.—W. H. Coffin, Sir John Conroy, Bart., M.A., Conrad W. Cooke, Major-General Festing, F.R.S., Prof. J. V. Jones, M.A., Prof. O. Lodge, D.Sc., F.R.S., Prof. W. Ramsay, Ph.D., F.R.S., W. N. Shaw, M.A., H. Tomlinson, B.A., F.R.S., and G. M. Whipple, D.Sc.

Votes of thanks were then passed (1) to the Lords of the Committee of the Council on Education for the use of the room in which the Society met; (2) to the Auditors, Prof. Minchin and Dr. Fison; (3) to the President and Officers of the Society for their services during the year.

The Meeting was then resolved into an Ordinary Science Meeting.

Messrs. E. W. Smith and C. E. Holland, B.A., were elected Members of the Society, and Mr. Sidney Evershed was proposed as a Member.

The paper on "*Galvanometers*," by Prof. W. E. AYRTON, F.R.S., Mr. T. MATHER, and Dr. W. E. SUMNER, was then resumed by Prof. AYRTON.

A long table of numbers accompanying the paper, and representing the result of experiments on many galvanometers, was explained. From this it appears that galvanometers of the D'Arsonval type were exceedingly efficient in proportion to the amount of wire used in the coils. It was for this reason that voltmeters with strong permanent magnets could be made sensitive, even with an exceedingly large external resistance in series, so as to diminish the power absorbed by the instrument. The space occupied by the wire was so exceedingly valuable that the extra resistance did not too much diminish the sensibility. The most sensitive galvanometers should therefore be made of the permanent magnet type. If, however, the magnets were to form part of the moving system, as in most galvanometers, the experiments showed that instruments of the Rayleigh, Gray, or Rosenthal type were the best. The coils should be numerous and small, as Mr. Boys had previously shown. As an astatic system of needles sets itself perpendicular to the earth's field, it was recommended that astatic galvanometers should be placed so that the needles pointed east and west. The controlling magnet would then not need to be turned round as it was raised or lowered. It was recommended to calibrate low resistance ballistic galvanometers for quantity by measuring the deflection for a known current. This obviates the necessity for large condensers or high potentials. The method, although not new, is not described in ordinary text-books. In conclusion, Prof. Ayrton asked for information with regard to microscope galvanometers.

Mr C. V. Boys, F.R.S., thought that the factor of merit of galvanometers should not be given in scale divisions per micro-ampère under the condition of constant controlling

moment. This gave too great an advantage to instruments of the Gray or Rosenthal type. Great sensibility could be obtained by diminishing the moment of inertia of the suspended parts, the practical limit being determined by the trouble due to the silk fibre. Spider lines, when used in place of silk fibres, gave better results. It was possible, by using a good suspending arrangement, to use needles $\frac{1}{8}$ " long, and a period of twenty seconds, and to gain a sensibility far greater than those indicated in the paper. Ballistic galvanometers should be made with needles as light as possible. The method proposed of winding the central part of the coil in the opposite sense to the rest would probably not be good, owing to the unevenness of the field produced. The conclusion came to by the authors that D'Arsonval galvanometers of great sensibility should be made with small coils placed in a very strong field, was one he had himself come to, but had finally abandoned, owing to difficulties caused by diamagnetism in the copper and to excessive damping due to Foucault currents.

Mr. SWINBURNE thought that the factor of merit of a galvanometer should be determined differently, according as it was to be used for the measurement of current, or quantity, or for null methods merely. He saw no great advantage in making practical instruments proportional. The name D'Arsonval should be dropped, as the instrument denoted by it was invented by Varley years ago. He would like to know the relative sensibility of the telephone and the Lippmann galvanometer.

Prof. FITZGERALD stated that Lord Rayleigh had shown that the microscope method of observing angular deflections was as sensitive as the ordinary method of mirror and scale, even when only the mirror was used as a pointer, so that if a pointer were attached it would be far more sensitive. The drawback, however, was that it was impossible to distinguish, with the microscope, between lateral displacements of the needles and the angular motion whose measurement was required. To get over this error it was necessary to read both ends of the pointer, but this was hard to do.

Prof. AYRTON replied to the different points raised in the discussion.

NOTICES OF BOOKS.

The Year-Book of Photography and Photographic News Almanack for 1890; containing the Results of Photographic Experimenting during the past Year, and Special Contributions by leading Photographic Authorities, Professional and Amateur; with a Portrait of Prof. E. Becquerel. London: Piper and Carter.

ONCE again the great and growing popularity of photography is brought to our notice, and once again we are compelled to admit that this art is being too little applied in one of the most desirable directions. We are told, indeed, that photography is "the handmaid of all the sciences, the servant of the geographer, engineer, and practical arts." But we find here nothing recorded as to any advances either in celestial or biological photography.

It may be asked whether M. Becquerel is not too strongly glorified in the passage:—"By studying with the spectroscopic light emitted by phosphorescent bodies he established a new method of spectrum analysis, which has of late been largely developed, and is employed to discover traces of substances which other methods of analysis do not suffice to make manifest." The development of phosphorescence spectroscopy, to which its great analytical value is due, may fairly be called a new departure.

Photography in natural colours, which, among photographers, plays the part of the decomposition of the elements among chemists, or the production of life *de novo* among biologists, is treated at some length. The writer's

point of view is to determine the relative merit of experimentalists in this direction, the palm being awarded to Becquerel as against Niepce de St. Victor.

The subject of Amateurs v. Professionals again comes forward. This question has its very life in the unfortunate predominance of portrait-photography. The more the art is applied to other purposes the more the difference between the two classes will fade away.

In connection with portraits we find some merited strictures on the growing evil of "re-touching." A photograph which has undergone this process neither throws any light on the character of the original, nor serves to prove his identity. Many of the articles here produced have so little bearing upon science and so much upon Art, that we feel incompetent to pronounce upon them. Did we make the attempt, we might lay ourselves open to severe castigation from the "Levites of Culture," who are waxing exceedingly rampant.

CORRESPONDENCE.

FRENCH ACCOUNTS OF JOSEPH PRIESTLEY.

To the Editor of the Chemical News.

SIR,—National jealousy and false pride prompt French historians of chemistry to belittle the work of Priestley and to magnify that of Lavoisier. Impartial and candid persons are willing to admit the claims for Lavoisier, who certainly had a genius for generalising and constructing an edifice of materials gathered by his contemporaries; but why the French writers so persistently distort certain facts in the life of Priestley which have no bearing on the scientific aspect is unaccountable. Georges Cuvier's attempt to show that Priestley's prime discovery—oxygen—was suggested by, or in consequence of, his hearing a memoir of Bayen on the reduction of mercuric oxide in closed vessels at the time of his visit to Paris, in company with Lord Lansdowne, is in accordance with the spirit of French historians (Cuvier, *Hist. des Sciences Naturelles*, Paris, 1843, vol. ii., p. 23).

Henri Gautier makes the following extraordinary statement; we give it in the original that we may not be charged with mistranslation:—

"Une larme aux malheurs de Priestley, qui fut persécuté toute sa vie. A Birmingham la populace pille et incendie sa maison puis court brûler sa campagne et sa bibliothèque. Son crime était de vouloir fêter dans un dîner notre 14 juillet. Réfugié au fond de l'Amérique du nord, il ne trouve pas le refuge même aux sources silencieuses de l'Usquehannah et demande un asile aux *peaux rouges*; enfin il meurt empoisonné avec toute sa famille" (*Essai sur l'Hist. Chimie*, Paris, 1837).

That Priestley was "persecuted all his life," that he "demanded a refuge at the hands of red-skins," and that "he and his whole family died by poison," are startling additions to our knowledge, and the latter clause must surprise his numerous descendants still living in England and America.

Gautier's statement is doubtless based on somewhat similar expressions of Dumas. In his "Leçons sur la philosophie chimique" (Paris, 1837), Dumas writes of Priestley thus:—"Incertain s'il ne devra pas aller demander l'hospitalité aux *Peaux rouges*"; and again: "Aux sources de Susquehannah, ou il acheta une terre de 200,000 acres. La, sous la protection du président Jefferson, il passa tranquillement le reste de ses jours, qui furent brusquement interrompus par un accident. Il fut empoisonné dans un repas avec toute sa famille, par une méprise dont ou ne s'est jamais rendu compte. Personne ne succomba, mais lui, déjà vieux et affaibli, ne put résister longtemps à l'inflammation d'estomac qui en fut la suite" (Second Edition, p. 131, Paris, 1878).

One need but consult the "Continuation of the Memoirs of Priestley by his Son" (London, 1806, two vols.), in which minute details of the chemist's last illness are given, to note how ridiculous is the account of his having died by poison (see pp. 207—222).

Ferdinand Hevefer repeats the story of the poisoning, but says this cause of illness was attributed without sufficient proof (*sans preuve suffisante*) (*Hist. de la Chimie*, Paris, 1869, vol. ii., p. 476).

Frémy, in his "Discours préliminaire sur le développement . . . de la chimie" (Paris, 1881), says Priestley died "dans une ferme isolée près des sources du Susquehannah," giving us a third variety of orthography for the rather puzzling Indian name Susquehannah.

The climax of absurdity is, however, attained by Benjamin Gastineau in his "Génies de la science" (Paris, n.d., 1870). After referring to his unhappy persecution in Birmingham, this author writes of Priestley:—"Dégoûté de son pays par ces scènes de cannibalisme il s'exila en Amérique où il s'éteignit paisiblement, après avoir été l'ami de Jefferson Davis" (p. 100).

The Birmingham riots of 1791 were assuredly disgraceful enough, and we would be the last to defend the instigators and their crimes, but to attribute *cannibalism* to Englishmen in 1791 is certainly a gross libel. Since, however, the author shows in the next sentence that he confounds President Thomas Jefferson with the late Jefferson Davis, what better things can be expected of him?

Though rather severe, we are almost ready to agree with the English librarian who remarked, when a certain bibliography was commended, "Is it by a Frenchman?" and receiving an affirmative reply, added "Then it must be a bad one!"—I am, &c.,

H. C. B.

ESTIMATION OF FATTY ACIDS IN ALIZARIN OIL.

To the Editor of the Chemical News.

SIR,—The CHEMICAL NEWS (vol. lxi., p. 52) contains a note on the above subject by Mr. F. Guthrie. There are several processes in use for the estimation of the oily matter, which is a factor in the valuation of the said oil, and these methods are liable to give very erroneous results, due to various causes. The one, I believe, mostly used is extraction by immiscible solvents, ether, chloroform, &c., and drying the immiscible layer on the bath *in vacuo*. Chloroform is, from various reasons, to be preferred, but it does not separate well. These methods, depending on extraction with solvents, give results in excess of the truth, due to mineral matter, which are more or less counterbalanced by the solubility of the sulpho-acids in water; nevertheless, in experienced hands, the results are not far from the truth. The method proposed by the writer is by no means new, and his procedure is improved as follows:—

The saponification of glycerides is ensured by digesting with alcoholic potash (on the steam-bath), instead of aqueous caustic soda, evaporation of the alcohol, and prolonged boiling with 20 c.c. of 1—5 H₂SO₄. Fatty acids are washed in usual manner.

After weighing, the fatty acids are then in a fit state for using in determining the acetyl and iodine values.

This process, if adopted, would give the best, and most accurate, results, and there could be no possible discrepancy between different operators as at present; but we must remember that the fatty matter in recovered in an entirely different form.

I shall have more to say on this subject when my work on Turkey Red Oil is completed.—I am, &c.,

J. ARTHUR WILSON.

Tottington, near Bury,
Feb. 3, 1890.

THE IGNITING-POINT OF SULPHUR.

To the Editor of the Chemical News.

SIR,—Recently, in the course of conversation, a remark was made on the low temperature at which sulphur ignites. My interlocutor fixed it as not far above the melting-point of the substance; I was incredulous, and we appealed to the authorities. The result of our joint investigation is as follows:—

- (1). "Gmelin," ii., 169. "Sulphur takes fire at 260° (C.) according to Dalton, at 294° according to Thomson."
- (2). Thomson, "System of Chemistry," i., 278. "When sulphur is heated to the temperature of 560° (F.=293° C.) it takes fire spontaneously."
- (3). Pelouze et Fremy, "Cours de Chimie Général," i., 23. "Il" (sulphur) "brûle dans ce gaz" (oxygen) "ou dans l'air à une température d'environ 150°" (C.).
- (4). Dumas, "Traité de Chimie," i., 127. "A 107° (C.) le soufre se liquéfie, et lorsqu'il est parvenu à 150°, sa surface, exposée au contact de l'air, s'enflamme."
- (5). "Watts," v., 532. "When heated in air or oxygen to a temperature of 250° C. takes fire."
- (6). "Miller," ii., 188 (Sixth Edition). "When heated in air it takes fire at between 235° and 260° (C.)."
- (7). "Tidy," Second Edition, p. 174, states that the octahedral variety fires at 239° F.=115° C., and the prismatic at 248° F.=120° C.

Thus, according to these chemists, sulphur ignites at quite a number of temperatures, ranging from 115° C. to 293° C., from which one is led to conclude that either it must be as protean in this respect as in its physical state, or (as a barely admitted alternative) one or more of these statements must be erroneous. It is possible that some one has it in his power to resolve this point, and to him I appeal, asking anyone who has actually determined the igniting-point of sulphur to give us the result, and indicate the method employed.—I am, &c.,

BERTRAM BLOUNT.

Laboratory, Broadway,
Westminster, S.W.
February 2, 1890.

TEA AND LARD.

To the Editor of the Chemical News.

SIR,—The CHEMICAL NEWS, vol. lxi., p. 59, contains a notice of the "Annual Report of the Analyst appointed for the Parish of Kensington for the year ending March 31, 1889," and in it remarks are made on the adulteration of tea, and the following words occur:—"Though not demonstrably adulterated, probably contained a proportion of leaves which had been previously exhausted and dried."

I should not have taken any notice of this were it not for the fact that I happen to know something of the cultivation and growth of tea, and its subsequent preparation for the market; and having examined this article in cities and towns under many circumstances, peculiar and otherwise, I think I can speak a little on the subject. Bearing in mind that good tea can be bought at a low price, I do not think it would pay for the trouble of collecting, drying, colouring, &c., of spent tea leaves, and I have never heard of these being collected for this purpose. It must be borne in mind that they (the leaves) must be manipulated in some way, otherwise they would be easily distinguished from other portions of a good tea. I know this sophistication was practised some twenty years ago; but if we find a little dirt, poor growth of leaves, and a little facing, it is about all we are likely to come across now-a-days. Yes, I think the faking up of exhausted tea leaves would hardly pay for the trouble, and we may consider ourselves fortunate that this article does not find more favour at the hands of the adulterator.

Then there is the aroma. I think the grateful herb is fairly treated in these times by the arch-fiend

sophisticator, and the poor may safely rely upon getting a pretty pure article, although at times it may be rather poor in quality, but this does not proceed from adulteration.

But with regard to lard, I can believe anything of this commodity; nothing would surprise me. It was but the other day that I had an interview with an individual who required some information respecting the refining of lard and the manufacture of margarine, and in the course of conversation I was asked whether it was possible to incorporate from 20 to 25 per cent of water in addition to "other matter," with lard. The addition was not considered an adulteration. I was told this lard was required for quick use in hotels, &c. I do not want to make a confession as to what I said, neither do I require absolution, but mention the matter as a fact. Most of us know that the lard we receive from America and elsewhere is, as a rule, a mysterious compound; its common adulterant is cotton-seed oil, but we may look for many other foreign bodies and find them, I would sooner use a common grade of margarine than most of the so-called refined lard. Housekeepers and others may be pretty sure what they get in the former case, but in the latter a shroud of mystery is around it, and I am surprised that more prosecutions do not take place; there's something wrong somewhere.—I am, &c.,

JOHN H. SWINDELLS, Ph.D.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 2, January 13, 1890.

Some New Fluorescences.—Lecoq de Boisbaudran.—The author has examined the fluorescence of mixtures of zirconia and Z β , of stannic acid and samaria, of tantallic acid and samaria, of the same two acids with Z α and Z β . He considers that the fluorescences described supply new instances of the plurality of the spectra obtained with one and the same active matter in different solid solvents.

The Relation between the Electric and Thermic Conductivities of the Metals.—Alphonse Berget.—The author does not believe that there is any absolute proportionality between the electric and thermic coefficients of conductivity. In a previous paper he has studied the variation of the thermic conductivity of mercury between 0° and 300°. He has found that the mean coefficient of variation is, for 1°, 0.00046, a number differing from the corresponding coefficient of variation of electric conductivity, which is 0.00085. The law of the proportionality of the two conductivities is therefore only approximately exact.

Formation—Heat of Platinic Chloride.—L. Pigeon.—The formation-heat of solid chloroplatinic acid, PtCl $_4$.2HCl + 6H $_2$ O, is 20.5 cal.

The Combinations of Gaseous Hydrogen Phosphide with Boron and Silicon Fluorides.—M. Besson.—Gaseous hydrogen phosphide, when very dry, seems to be without action upon boron fluoride at the ordinary temperature; but if the two gases are let come in contact in a refrigerated receiver, combination takes place at about -30°. At -50° a white solid is deposited, which takes a yellow tint as the temperature rises, and becomes decomposed. The compound may be represented by the formula 2BF $_3$ + PH $_3$. A direct combination of hydrogen phosphide with silicon fluoride requires a temperature of -22° and a pressure of about 50 atmospheres. These

compounds increase the analogy between hydrogen phosphide and ammonia.

Observation on the Rotatory Power of Matezite and Matezodambrose.—Aimé Girard.—The identity of the rotatory power of matezite and matezodambrose is absolutely confirmed.

On a New Inosite, Racemo-inosite.—M. Maquenne and Ch. Tanret.—The two inosites have an exactly equal rotatory power, but in opposite directions. This equality of rotatory power in an inverse direction is found in their acetic ethers, which are equally amorphous, and soften at the heat of the hand. They melt at 247°. They behave exactly in the same manner with reagents.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. viii., No. 1.

Recent Improvements in the Electro-Metallurgy of Aluminium, and on the Influence of this Metal upon Siderurgic Products.—Van Langhen.—Aluminium renders iron softer, and naturally increases considerably the force of transverse resistance of white cast-iron, which is ordinarily porous. It also improves grey cast-iron, though to a less extent. The presence of aluminium has a still greater effect in augmenting the resistance to shocks. Aluminium augments the elasticity and diminishes the strain due to internal tension.

New Process for Carbonising Wood for the Manufacture of Powder.—Herr Güttler proposes to inject into the retorts hot carbonic acid during the process of manufacture and cold carbonic acid during the refrigeration. The gases from lime-kilns may be used for this purpose.

Journal für Praktische Chemie.
New Series, Vol. xl., No. 17.

Researches from the Laboratory of the University of Freiburg.—These researches comprise a memoir by Fr. Kehrman on the Influence of the Nature and Position of certain Atoms and Atomic Groups in the Benzol Nucleus upon the Replaceability of Quinone-Oxygen by the Isonitroso-Group, and a paper by C. Willgerodt on the Symmetric Nitrophenyl Hydrazines of the Aromatic Series.

Fluorine Compounds of Vanadium and its Nearest Analogues.—Emil Petersen.—The author describes the potassium and ammonium double fluorides of vanadium.

Action of Nascent Nitrous Acid upon Various Amines and Phenoloid Bodies.—A. Deninger.—The author gives an account of the reaction of nascent nitrous acid with aniline, orthotoluidine, paratoluidine, parabenidine, paratoluidine, the naphthylamines, sulphanilic acid, salicylic acid and its esters, and paraphenolsulphonic acid.

On Oxymiazine (Oxypyrimidine).—E. von Meyer.—The author corrects two errors in his paper on the polymerisation of the nitriles (*Journal Prakt. Chemie*, xxxviii., p. 336; and xxx., 188 and 202), i.e., the statements on the melting-points of amido- and of oxymethylphenylmiazine. The former melts, not at 172°, but at 168°, and the latter not at 256°, but at 250°.

MEETINGS FOR THE WEEK.

- MONDAY, 17th.**—Medical, 8.30.
Society of Arts, 8. "Stereotyping," by Thomas Bolas, F.C.S.
TUESDAY, 18th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
Institute of Civil Engineers, 8.
Pathological, 8.30.
Society of Arts, 5. "Ocean Penny Postage and Cheap Telegraph Communication between England and all parts of the Empire and America," by J. Henniker Heaton, M.P.

WEDNESDAY, 19th.—Society of Arts, 8. "The Organisation of Secondary and Technical Education in London," By Prof. Silvanus P. Thompson, D.Sc.

Meteorological, 7.
THURSDAY, 20th.—Royal, 4.30.
Royal Society Club, 6.30.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "The Three Stages of Shakespeare's Art," by Rev. Canon Ainger, M.A., LL.D.

Chemical, 8. "The Behaviour of the more Stable Oxides at High Temperatures," by G. H. Bailey, D.Sc., and W. B. Hopkins. "The Influence of Different Oxides on the Decomposition of Potassium Chlorate," by G. J. Towler, M.Sc., and J. Grant.

FRIDAY, 21st.—Royal Institution, 9. "Magnetic Phenomena," by Shelford Bidwell, M.A., F.R.S.

Geological, 1. (Anniversary).
Physical, 5. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes. "The Geometrical Construction of Direct Reading Scales for Reflecting Instruments," by A. P. Trotter, B.A. "A Parallel Motion suitable for Recording Instruments," by A. P. Trotter, B.A. "On Bertrand's Refractometer," by Prof. S. P. Thompson.

SATURDAY, 22nd.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

MACHINERY FOR SALE.

Four 27-inch 36 Chamber High-Pressure
Filter, Pressers, and Receivers, with Iron Columns, Stand-pipes, and Connections.
Seven Wood Vats, 11 feet 10 inches long, 3 feet 10 inches wide, and 3 feet 6 inches deep.
Two Wood Vats lined with Sheet Lead, 11 feet 9 inches long, 3 feet 9 inches wide, and 3 feet 7 inches deep.
Two Wood Vats, 11 feet 10 inches long, 5 feet 5 inches wide, 3 feet 6 inches deep.
Two Wrought-Iron Tanks, 10 feet long, 3 feet wide, and 3 feet deep.
One Hoist with Chains and Fittings complete.
One Levigating Pan with Edge-Runners.
One Blackman Air-Propeller and Fittings.
Quantity of Iron Racks suitable for Drying Stoves.
One Disintegrator with Toothed Crushing Mill and all Fittings.
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The Directors of the SOUTHAMPTON GAS LIGHT AND COKE COMPANY desire to receive Tenders for Surplus TAR and AMMONIACAL LIQUOR for One Year from the 6th March, 1890.

Estimated yearly make:—Tar, 250,000 gallons; Ammoniacal Liquor, 500,000 gallons.

The Contractor must agree to remove the same whenever required, and not to allow an accumulation of more than 10,000 gallons of either Tar or Liquor. Tank trucks and barges can be loaded at the Company's wharf.

Prices to be given for Liquor from 8 to 16 ounces per 1000 gallons. Strength to be ascertained by the Distillation Process of Mr. F. W. Hartley, A.I.C.E.

Prices for Tar to be per gallon.
Payments to be made in cash, fortnightly.
The successful Contractor will have to sign Agreement and Bond for the due performance of his Contract.

Tenders to be delivered to the undersigned not later than 10 o'clock in the morning of the 5th March, 1890. The Directors do not pledge themselves to accept the highest or any Tender.

C. CROWTHER SMITH, Secretary.

Ogle Road, Southampton,
February 12, 1890.

Silicates of Soda and Potash in the state of Soluble Glass, or in CONCENTRATED SOLUTION of first quality, suited for the Manufacture of Soap and other purposes, supplied on best terms by W. GOSSAGE and Sons, Soap Works, Widnes, Lancashire.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1578.

NOTE ON THE DISPLACEMENT OF SILVER BY PLATINUM AND PALLADIUM.

By FRANK P. PERKINS, F.I.C.

I HAVE observed that it is sufficient to add to a slightly acidulated solution of platinic chloride a fragment of sodium sulphite, and then brush the liquid over a well-washed silver print produced on plain salted paper, for the silver to be almost immediately displaced by platinum. This is a simple method of "toning" for such as have not the ready formed platinous salt at hand.

I have also noticed that a slightly acidulated solution of palladous chloride may be used in the same way, and with similar results.

Exeter, Feb. 13, 1890.

CELLULOSE AND ALKALIES : CELLULOSE BENZOATES.

By C. F. CROSS and E. J. BEVAN.

A RECENT observation that the hydrated modifications of cellulose precipitated from solution either in the ammonia copper reagent, or in $ZnCl_2$.Aq. (50 per cent), are soluble in strong solutions of sodium hydrate, has afforded a ready means of preparing benzoates of cellulose. By treatment of the alkaline solution with benzoic chloride (Bau mann, *Ber.*, xix., 3218) these derivatives are formed and precipitated. They are soluble in glacial acetic acid. On adding water to the solution they are precipitated in voluminous white flocks. The analysis of these compounds by alkaline hydrolysis, and estimation of the benzoic acid by titration, has occasioned some difficulty, and we defer, for the present, any statements as to their composition. They are fusible at high temperatures; on continuing to heat, benzoic acid sublimes. We hope to complete our present investigation of these compounds at an early date.

A noteworthy property of these hydrated modifications of cellulose is that they are assimilable by microscopic organisms. That they form an excellent nidus, e.g., for moulds, appears from the fact that a quantity of the moist substance, well washed after precipitation, squeezed, and kept in a loosely covered jar, has developed an abundant growth of several varieties of these organisms.

In relation to any definitions of cellulose involving resistance to alkalies, these results have a special significance. Growing plants certainly afford an infinite variety of such hydrates, which, not less certainly, will be less or more soluble in alkaline solutions.* The cellulose isolated as the residue of processes of oxidation and hydrolysis must therefore be to that extent an arbitrary quantity. Believing these facts to be generally recognised, we are not a little surprised to read a paper by Lange in the *Ztschr. Physiol. Chemie*, p. 281 of the current issue, basing "A Method for the Quantitative Estimation of Cellulose" upon the observation of Hoppe-Seyler that cellulose resists the action of strong solutions of the alkaline hydrates at 200°. The essential part of the author's proposed process—as applied to woods—consists in a digestion with three to four times the weight of alkaline hydrate dissolved in an equal weight of water, with a

gradual increase of temperature to 180°, at which point it is maintained for one hour.

Of course, in view of the fact that the wood substance is a complex anhydride and a compound of cellulose and lignone "residues," the net product of the complex changes which must take place may very well be a cellulosic aggregate, approximating in weight to that of the pure cellulose isolated by the simple and definite process of converting the lignine into its chloride and removing the derivative by treatment with the specific solvent, sodium sulphite (solution). The author's results are interesting as a study of the action of the alkalies upon the ligno-celluloses (these results, as regards the soluble products, form, in fact, the substance of two valuable communications in the same journal); but we fail to see, more especially in absence of any evidence as to the composition of the residues ("cellulose"), that such a process of estimating cellulose is anything but a retrograde advance.

In view of the results described in this communication, and the solubility of the typical cotton cellulose, when hydrated, in alkalies, the author will probably see fit to revise some of his conclusions.

A PTOMAINE EXTRACTED FROM URINE IN A CASE OF INFECTIOUS DISEASE ("MUMPS").

By A. B. GRIFFITHS, Ph.D., F.R.S.E., &c.

IN a case of "mumps" where the kidneys were involved an alkaloid was extracted from the urine by what may be called the "ether-tartaric acid" or the Luff method. The process is as follows:—

- A considerable quantity of the urine is made alkaline by the addition of a solution of sodium carbonate, and then agitated with half its volume of ether.
- The ethereal solution (after standing) is filtered and agitated with a solution of tartaric acid. The tartaric acid combines with any alkaloids present, forming soluble tartrates; and the solution of tartrates forms the lower layer of the liquid mass.
- The tartaric acid solution (after being separated from the ether) is also made alkaline by the addition of sodium carbonate, and is once more agitated with half its volume of ether.
- The ethereal solution (after standing) is separated, and the ether allowed to evaporate spontaneously.
- The residue (after drying over sulphuric acid) is finally examined for alkaloids (ptomaines).

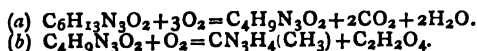
The alkaloid extracted by the above method (in a case where the parotid and submaxillary glands were both affected) crystallises in white prismatic needles, which are soluble in water, ether, and chloroform. It has a neutral reaction and a slightly bitter taste. It forms a yellow crystalline platinochloride, a pale yellow aurochloride, and a white crystalline hydrochloride. It combines with phosphomolybdic acid, forming a golden yellow precipitate. This alkaloid produces a white precipitate with phosphotungstic acid, a slight yellow precipitate with mercuric-potassic iodide, a brown precipitate with iodine solution, and a flocculent precipitate with picric acid. Analyses of the alkaloid in question gave the following results:—

	Found.			Calculated for $C_6H_{13}N_3O_2$
	I.	II.	III.	
Carbon	45.34	—	45.29	45.28 p.c.
Hydrogen	8.22	—	8.20	8.17 "
Nitrogen	26.39	26.42	—	26.41 "
Oxygen	—	—	—	20.12 "

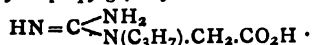
The above figures correspond with the formula $C_6H_{13}N_3O_2$.

* cf. "Hydration of Cellulose," *J. Soc. Chem. Ind.* 1885, p. 7.

When boiled with mercuric oxide this base yields creatine (methylglycocycamine), and finally methylguanidine and oxalic acid:—

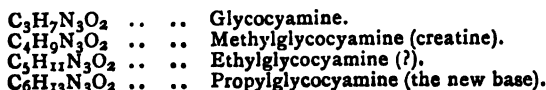


Therefore this alkaloid is related to creatine (an animal product) or methylglycocycamine, as well as guanidine. It may possibly be *propylglycocycamine*:—



Further research will settle this point.

If the alkaloid is propylglycocycamine we have the basis of a homologous series of oxygenated bases related to the ureides. Thus—



The new animal alkaloid is poisonous. When administered to a cat it produced nervous excitement, cessation of the salivary flow, convulsions, and death.

The alkaloid in question is not found in normal urines, therefore there is no doubt that it had been produced within the system during the course of the disease.

It is difficult to say how this alkaloid is formed; it may be a morbid leucomaine (a product of vital physiological or rather pathological processes), or it may be formed from the decomposition of albumenoid molecules by the agency of pathogenic and other microbes.

THE TREATISE OF DEMOCRITUS ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

LITTLE apology is needed to English readers for publishing the earliest known chemical treatise for the first time in English. It is a work on the manufacture of gold and silver, and the receipts are entirely practical ones, which can be followed out at the present time, and which produce alloys or superficial imitations of those metals. The idea of transmutation does not explicitly occur in the work.

Democritus lived in the Fourth Century, B.C. The work proceeds from writers of his school, and is certainly not later than the first centuries of our era. A somewhat magical introduction is prefixed in the text of M. Berthelot.

There were originally four books on the tincture of purple, gold, silver, and stones. Of these, we have the second and third and a fragment of the first.* The text I translate from is the Latin translation of Pizzimenti, published at Cologne, 1574, and Padua, 1575, with ancient commentaries. The English reader may see a sample of these at the end of the translation of Basil Valentine, London, 1678, 8vo. The commentators have well fulfilled their aim; they have explained words and letters, until the plain statements of their author are buried under a mountain of verbiage.

I have chosen this text to bring out the differences between it and the Greek text, first published by M. Berthelot in his "Collection of Ancient Greek Alchemists," Paris, 1888, a work to which I am under great obligations, and to which I would refer any student interested in the study of alchemy. The variations (not merely verbal) I have indicated by italics. A glossary, with references to Pliny's "Natural History," is appended.

ROBERT R. STEELE.

3, Blomfield Terrace,
Shepherd's Bush, W.

* Published in the CHEMICAL NEWS, vol. xlviii, p. 279.

FRAGMENT OF ANCIENT INTRODUCTION.

"Nature rejoices with Nature; Nature conquers Nature; Nature restrains Nature."

We (his disciples) greatly wondered at how briefly he had bound up the whole science. I come into Egypt, bearing the treatises of nature,* that thou mayest cast off confused and superfluous matter.

I. COPPER IS WHITENED WITH MERCURY-AMALGAM OR ARSENIC, AND IS THEN COLOURED GOLDEN BY ELECTRUM OR POWDERED GOLD.

Taking mercury, thrust it into the body† of magnesia, or into the body of Italian antimony, or of unfired sulphur, or of *silver spume*, or of quick lime, or to alum from Melos, or to arsenic, or as thou knowest, and throw in *white earth of Venus*,‡ and thou shalt have clear *Venus*; then throw in yellow *Luna*, and thou shalt have gold, and it will be chrysocoral reduced into a body.

Yellow arsenic also makes the same, and prepared sandarach, and well bruised cinnabar, but quicksilver alone makes brass shining; for nature conquers nature.

II. SULPHIDE OF SILVER IS TREATED WITH SULPHIDES OF LEAD OR ANTIMONY, AND THE RESULTING ALLOY IS COLOURED GOLDEN.

Treat silver marcasite, which is also called siderites, and do what is usual that it may be melted. It melts with *yellow* or white litharge, or in Italian antimony, and cleanse it with lead (not simply, say I, lest thou err, but with that from *Seissile*, and our black litharge), or as thou knowest; and heat, and throw it made yellow to the material,§ and it becomes coloured; for nature rejoices with nature.

III. COPPER PYRITES IS ROASTED AND TREATED WITH SALT AND ALLOYED WITH SILVER OR GOLD TO FORM GOLD-COLOURED ALLOYS.

Treat pyrites till it becomes incombustible, casting off darkness, but treat with brine, or fresh urine, or sea water, or oxymel, or as thou knowest, until it becomes as an incombustible shaving of gold; and as it becomes so, mix with it unfired sulphur, or yellow alum, or Attic ochre, or what thou knowest, and add to *luna* for sol, and to sol for auriconchylum; for nature conquers nature.

IV. CLAUDIAN METAL IS RENDERED YELLOW BY SULPHUR OR ARSENIC, AND ALLOYED ON GOLD OR SILVER.

Taking claudianum, thou shalt make a marble, as of custom, until it becomes yellow. Thou shalt not render the stone yellow, I say, but that which is useful of the stone. Thou shalt yellow it with alum burnt with sulphur, or with arsenic, or sandarach, or lime, or that thou knowest, and if thou apply it to *luna* thou makest sol, but if to sol thou makest auriconchylum; for victorious nature restrains nature.

V. SILVER OR BRONZE ARE TREATED WITH AN AMALGAM OF IRON TO PRODUCE GOLD OR ELECTRUM.

Make cinnabar white by oil, or vinegar, or honey, or brine, or alum, then yellow by misy, or sory, or chalcant, or live sulphur, or that thou knowest, and add to *luna* and it will be sol if thou colourst golden, or to bronze for electrum. Nature rejoices with nature.

VI. A YELLOW GOLDEN VARNISH FOR METALS.

Whiten, I say, *copper*, *cadmia*, or *sonytes*, as of custom, afterwards make it yellow. But you will yellow it with the bile of a calf, or terebinth, or castor oil, or radish

* "Nature" seems to be used for the specific qualities of a substance; those which differentiate it from others.

† Probably, the reduced metal of.

‡ Berthelot's text rarely uses these alchemical names, never in the case of copper.

§ For colouring the alloy—not expressed.

oil, or yolks of eggs, which can render it yellow, and add to *luna*, for it will be gold for gold*; for nature conquers nature.

VII. THE TREATMENT OF SILVER BY SUPERFICIAL SULPHIDATION TO RENDER IT GOLD COLOURED.

Treat androdamas with bitter wine, or sea water, or acid brine, which things can attack its nature, melt with Chalcidonian antimony, and treat it again with sea water, or brine, or acid brine; wash until the blackness of the antimony goes away, heat or roast it until it begins to grow yellow, and thou shalt treat with untouched *divinet* water, and lay it on silver, and when thou addest live sulphur thou makest chrysosomium into golden liquid; for nature conquers nature. This is the stone called chrysites.

VIII. AN ALLOY OF COPPER AND LEAD IS FORMED, WHICH IS TURNED YELLOW.

Taking white earth from ceruse, I say, or from the scoria of silver, or of Italian antimony, or of magnesia, or even of white litharge, whiten it with sea water, or acid brine, or with water from the air under the dew, I say, and the sun, that it, when dissolved, may become white as ceruse. Heat then this in the furnace, and add to it the flowers of copper, or scraped rust of copper, worked up by art, I say, or burnt bronze sufficiently corroded, or chalcites, or *cyanum*; then it becomes compact and solid, but it becomes so easily. This is molybdochalum. Test it therefore, whether it has cast off its blackness, but if not, blame not the bronze, but rather thyself, since thou hast not conducted the operation rightly; therefore thou shalt brighten it, and dissolve it, and add what is necessary to yellow it, and roast till it begins to grow yellow, and throw it into all bodies; for bronze colours every body where it is shining and yellow; for nature conquers nature.

IX. COPPER AND SILVER ARE MADE YELLOW BY SULPHATE OF IRON; WITH A PROCESS OF CEMENTATION.

Rub up sory and chalcant with unfired sulphur; but sory is, as leprous cyanus, always found in misy; they call it green chalcant. Roast it, therefore, in the middle of coals for three days, until it becomes a red drug, and throw it into Venus, or Luna made by us, and it will be Sol. Place this, cut up in sheets, in vinegar, and chalcant, and misy, and alum, and sal cappadociae, and red nitre, or as thou knowest, for three, or five, or six days, until it becomes a rust, and it tinges; for chalcant makes sol a rust. Nature rejoices with nature.

X. AN ALLOY OF GOLD IS HEATED BY SUPERFICIAL CEMENTATION.

Treat Macedonian chrysocola, which is like the rust of bronze, by dissolving it in the urine of a young girl until it entirely changes; for the nature is hidden within. When, therefore, it is changed, dip it into castor oil, often heating it, and tinging it, afterwards roast with alum, first dissolving with misy or unfired sulphur; render it yellow, and colour the whole body of gold.

(To be continued).

Combinations of the Alkaline Metals with Ammonia.—M. Joannis.—The author has already shown that an excess of ammoniacal gas gives, with the alkaline metals, a solution possessing a variable tension as long as the concentration does not reach $\text{Na} + 5.3\text{NH}_3$ at 0°, then a constant tension whilst ammonia is withdrawn, and NH_3Na crystallises. The results of experiments do not agree with the theoretical conclusions of M. Bakhuis Roozeboom.—*Comptes Rendus*, Vol. cx., No. 5, February 3, 1890.

* Greek reads:—"Gold, for it will be golden through gold and the golden liquor."

† A curious mistranslation, the words *divine* and *sulphur* being similar in Greek. It is probably a polysulphide of calcium.

ON THE
DECOMPOSITION OF ORGANIC MATTER
IN WATER.*

By MARK POWERS.

(Concluded from p. 79).

Other Nitrogenous Substances.

In the following Table I have given the results of my experiments, showing how much of the total nitrogen can be evolved as ammonia by the ordinary Wanklyn method from an important class of nitrogenous compounds.

1 m.grm. substance.	M.grms. NH_3 evolved.	Theoretical amount.
Leucine, $\text{C}_6\text{H}_{13}\text{NO}_3$	0.130	0.130
Glycocoll, $\text{C}_2\text{H}_5\text{NO}_2$	0.225	0.226
Aspartic acid, $\text{C}_4\text{H}_7\text{NO}_4$	0.125	0.130
Indol, $\text{C}_8\text{H}_7\text{N}$	0.144	0.145
Skatole, $\text{C}_9\text{H}_9\text{N}$	0.120	0.130
Tyrosine, $\text{C}_9\text{H}_{11}\text{NO}_3$	0.094	0.094
Urea, $\text{CH}_4\text{N}_2\text{O}$	0.060	0.058
Hippuric acid, $\text{C}_9\text{H}_9\text{NO}_3$	0.090	0.095
Asparagine, $\text{C}_4\text{H}_8\text{N}_2\text{O}_3 + \text{H}_2\text{O}$	0.200	0.226
Quinine sulphate, $(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)_2\text{H}_2\text{SO}_4 + 8\text{Aq}$	0.040	0.080
Quinidine sulphate, $(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)_2\text{H}_2\text{SO}_4 + 2\text{Aq}$	0.043	0.071
Strychnine, $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$	0.097	0.101
Trimethylamine chlor., $\text{C}_3\text{H}_7\text{NH}_2\text{HCl}$	0.180	0.178
Aniline chloride, $\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$	0.060	0.131
Albumen	0.149	0.157

In this list of compounds the intention has been to include the important decomposition products of albumen, such as leucine, tyrosine, aspartic acid, glycocoll, indol, and skatole, as the greater portion of the organic nitrogen of natural waters occurs as a constituent of derived products from albuminous matter. Tiemann and Preusse have obtained the total amount of nitrogen in leucine, tyrosine, and aspartic acid in the form of ammonia. My own experiments gave similar results in case of each substance mentioned, the total nitrogen being obtained by the first distillation.

Hippuric acid decomposes in a very peculiar manner. 3 m.grms. of this acid were dissolved in 500 c.c. of water, 200 c.c. were distilled for free ammonia, 50 c.c. permanganate solution added, and the albumenoid ammonia obtained was 0.02, 0.03, 0.042, 0.05, 0.043 m.grms. in the different distillates; a second distillation gave 0.065, 0.008, 0.002 m.grms., thus completing the evolution of the total nitrogen in the form of ammonia.

Wanklyn states that quinine, quinidine, strychnine, &c., yield one-half their nitrogen in the form of ammonia. I have obtained similar results in case of quinine and quinidine, but the sample of strychnine tested gave nearly the whole amount.

The Oxidation of Organic Matter in Water by
Means of Permanganate Solution.

The extent to which a large number of important organic compounds are oxidised, especially the principal

* *Journal of Analytical Chemistry*, Vol. iii., Part 4, October, 1889.

decomposition products of albumen, is shown in the following table. The methods of Schulze and Kubel are compared by giving the results of each. In Schulze's method 100 c.c. of water containing a definite amount of the compound is boiled during ten minutes with constant excess of standard potassium permanganate solution (containing 320 m.grms. per litre) and a definite quantity of pure sodium hydrate, while in Kubel's method the substance is boiled during ten minutes in solution acidified with sulphuric acid. By either method the amount of oxygen consumed varies from a mere trace to almost the total amount necessary for complete oxidation. The correction necessary in Schulze's method was determined by making blank experiments.

1 m.grm. substance.	Schulze's method. M.grms. oxygen consumed.	Kubel's method. M.grms. oxygen consumed.	M.grms. oxygen required for com- plete oxidation.
Leucine, $C_6H_{13}NO_3$	0.216	0.208	2.015
Tyrosine, $C_9H_{11}NO_3$	1.224	1.320	1.812
Clycocol, $C_2H_7NO_2$	0.100	0.100	0.960
Aspartic acid, $C_4H_7NO_4$	0.368	0.368	0.902
Asparagine, $C_4H_8N_2O_3 + H_2O$	0.112	0.08	0.960
Indol, C_8H_7N	1.252	2.080	2.666
Skatole, C_9H_9N	1.696	1.720	2.748
Benzoic acid, $C_7H_6O_2$	0.026	0.096	1.967
Urea, CH_4N_2O	trace	trace	0.800
Hippuric acid, $C_9H_9NO_3$	0.224	0.228	1.743
Trimethylamine chloride, $C_3H_7NH_2HCl$	0.024	0.032	1.761
Aniline chlor., $C_6H_5NH_2HCl$	1.312	1.320	1.916
Salicylic acid, $C_7H_6O_3$	1.392	1.480	1.623
Quinine sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8Aq$	0.480	0.820	1.798
Quinidine sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 2Aq$	0.416	0.752	2.046
Cinchonine sulphate, $(C_{19}H_{22}N_2O)_2H_2SO_4 + 2Aq$	0.440	0.744	2.127
Cinchonidine sulphate, $(C_{19}H_{22}N_2O)_2H_2SO_4 + 6Aq$	0.400	0.640	1.964
Strychnine sulphate, $(C_{21}H_{22}N_2O_2)_2H_2SO_4 + 6Aq$	0.872	1.048	1.867
Morphine chlor., $C_{17}H_{19}NO_3HCl + 3Aq$..	1.016	1.062	1.726
Tannic acid, $C_{14}H_{10}O_9 + 2Aq$	0.768	0.797	1.073
Citric acid, $C_6H_8O_7$	0.504	0.490	0.750
Tartaric acid, $C_4H_6O_6$	0.368	0.432	0.533
Starch, $C_6H_{10}O_5$	0.540	0.544	1.185
Cane sugar, $C_{12}H_{22}O_{11}$	0.628	0.636	1.123
Lactose, $C_{12}H_{22}O_{11} + H_2O$	0.640	0.640	1.066
Glucose, $C_6H_{12}O_6$	0.650	0.648	1.066

From the results of these experiments, Kubel's method being simpler, has the preference. The results obtained by the two methods are in most cases approximately the

same. A large number of the above compounds require over one-half of the amount of oxygen necessary for complete oxidation. In several instances these results accord with those given by Tiemann and Preusse, while in others, different figures were obtained. Without doubt, the application of the principle of oxidation, according to the methods detailed above, yields more satisfactory information than any other so far proposed. Dr. Frankland states that cane-sugar and starch do not require so much as one-hundredth of the oxygen necessary for total oxidation; by Kubel's method, the quantity is over one-half the amount required. In other cases the oxidation would be slight at the ordinary temperature, while at the boiling point of water a large amount of oxygen would be consumed.

In conclusion, several statements may be made in reference to the results obtained by these experiments.

Albumen, urea, and some other compounds will evolve their total nitrogen in the form of ammonia by prolonged boiling with strong solution of alkali permanganate.

No definite portion of the total nitrogen of these compounds is obtained in the first distillation, the amount depending upon a number of conditions, of which the quantity of substance used and the rapidity of distillation are the chief factors that vary the result. Albumen gave in one experiment by the first distillation 1.42 m.grms. ammonia, while the total amount was 2.8 m.grms.; in a second experiment 2.63 m.grms.—total, 4.63 m.grms. In one instance, thirteen successive distillations were made, collecting four distillates of 50 c.c. each, the total amount obtained being about 95 per cent. Egg albumen undergoing putrefaction yields a gradually increasing quantity of free ammonia, while the albumenoid ammonia decreases in a regular manner.

The principal decomposition products of albumen give up readily their total nitrogen in the form of ammonia. Indol and skatole are carried over in the distillation of free ammonia, and give a milkiness to the solution when nesslerised. This fact may account in part for the "haziness" frequently observed in nesslerising.

2.5 m.grms. urea gave of free and albumenoid ammonia 15.5 per cent, while $\frac{1}{2}$ m.grm. yielded 25 per cent. Urea was boiled ten hours with strong solution of alkali permanganate, but not completely decomposed. Complete decomposition was effected, however, by boiling 2 m.grms. during twenty hours with 50 c.c. of permanganate solution. On the other hand, 2 m.grms. of this compound were almost completely decomposed by boiling in water alone for same length of time. The amount of ammonia evolved from urea by the ordinary method depends upon the amount of this substance in solution, a smaller quantity yielding a relatively larger quantity of both free and albumenoid ammonia.

Hippuric acid yields more albumenoid ammonia in the last distillate than in the first. It is, however, completely decomposed by a second distillation.

Quinine and quinidine yield apparently about one-half of their total nitrogen in the form of ammonia. The sample of strychnine tested gave nearly the total amount.

The amount of oxygen consumed varies from a mere trace to almost the total amount required by theory. About one-half the number of compounds studied required from one-half to seven-eighths of the total amount of oxygen. Indol, skatole, and tyrosine strongly reduce the permanganate solution. A large number of organic compounds containing no nitrogen, such as the sugars, alcohols, vegetable acids, &c., are stronger reducing agents than some nitrogenous compounds which may be considered more dangerous.

No compounds were examined, except urea, which did not consume more or less oxygen.

For many valuable suggestions while engaged in the study of these compounds, I am deeply indebted to Dr. John H. Long, in whose laboratory these experiments have been made.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Percival Babington, Elmfield, Rotherham, Yorks; Richard Berncastel, 38, Ventnor Villas, Brighton; William Burton, 18, Victoria Street, Basford, Stoke-on-Trent; John Dennatt, Lyndhurst Crescent, Glenferrie, Melbourne; Frank Gosling, Waldegrave Road, Teddington; John Charles Jackson, 51, Wellington Road, St. John's Wood, N.W.; Alfred E. Macintyre, Saint John, N.B., Canada; Ira Moore, Sutton Crosshills *via* Keighley; John Myles, Butterburn Park, Hamilton.

The following were elected Fellows of the Society:—

Edward Whitley Allsom, James Munro Taylor Anderson, Frederick Graham Ansell, George Frederick Brindley, Sydney Hoare Collins, John B. Coppock, Thomas Southall Dymond, Alexander Charles Farquharson, Cuthbert Chapman Gibbs, James Grant, William Winsor Haldane Gee, B.Sc., P. J. Hartog, Joseph H. Heywood, Arthur Hutchinson, Robert Law, James Guthrie Mactaggart, Arthur Hotham McConnell, Hugh Marshall, Francis Herbert Mason, William Samuel Newman, Edgar Philip Perman, B.Sc., Edward Russell, William Charles Sayers, Saville Shaw, Harry Wood Smith, B.Sc., Henry Heron Smith, John Stokes, John Wade, James Walker, Sydney Russell Wells, B.Sc.

The following papers were read:—

4. "Observations on Nitrous Anhydride and Nitrogen Peroxide." By Professor RAMSAY, Ph.D., F.R.S.

The author recommends as the best method of preparing pure nitrogen peroxide that the deep blue-green liquid, supposed to be a mixture of this oxide and nitrous anhydride, which is obtained by condensing the products of the interaction of arsenious oxide and nitric acid, be added to a solution of nitric anhydride in nitric and phosphoric acids, prepared by adding phosphoric anhydride to well cooled nitric acid; after agitating the mixture, the upper layer is decanted and distilled. He assumes that the two oxides interact thus: $N_2O_5 + N_2O_3 = N_2O_4$.

The melting-point of the peroxide was found to be $10^{\circ}14'$, in agreement with Deville and Troost's statement. The depression in the freezing-point caused by one part of chloroform in 100 parts of the peroxide was $0^{\circ}35'$, and by one part of chlorobenzene, $0^{\circ}37'$: the molecular depression is therefore 41° .

The heat of fusion (W) of the peroxide, calculated from this number and the observed fusing-point by Van't Hoff's formula—

$$W = \frac{0.02T^2}{t},$$

where T is the freezing-point of the solvent in absolute degrees and t the molecular depression, is 33.7 cal.; a direct determination gave 32.3 .

To determine the molecular weight of nitrous anhydride, a known weight of nitric oxide was passed into the peroxide, and the depression of the freezing-point determined; assuming that an amount of nitrous anhydride equivalent to the nitric oxide was formed, the results gave the values 80.9 , 92.7 , and 81.0 , instead of 74 , the value corresponding to the formula N_2O_3 . The author was unsuccessful in freezing nitrous anhydride, even at -90° , by means of liquefied nitrous oxide. It was found to be soluble in this liquid, and it was further observed that as evaporation took place nitric oxide gas was given off, together with the nitrous oxide: it would therefore appear that N_2O_3 is unstable, even at the very low temperature at which nitrous oxide is liquid.

DISCUSSION.

Referring to Professor Ramsay's determination of the heat of fusion of nitrogen peroxide, Mr. PICKERING said that observations on substances which exercise an appreciable influence on each other cannot be safely used in deducing the heat of fusion. Thus, in the case of mixtures of water and sulphuric acid solutions containing 29.5, 18.5, 8.6, 1.0, and 0.07 per cent of acid gave respectively the values 37.4 , 58.3 , 79.9 , 74.9 , and 56.3 as the heat of fusion of water, instead of 79.6 . In strong solutions the lowering of the freezing point is always abnormally great; in such solutions, according to the theory of osmotic pressure, the dissolved molecules, being more subject to each other's attraction, should exercise less attraction on the molecules of the solvent, and these latter, therefore, should coalesce more readily to form a solid.

Mr. GROVES remarked that sulphuric acid might be used in preference to phosphoric anhydride in preparing pure nitrogen peroxide: the liquid product obtained by warming arsenious oxide with a mixture of two parts nitric and one of sulphuric acid might be freed from the small proportion of nitrous anhydride which it contained by treatment with sulphuric and a little nitric acid, and on then distilling, pure nitrogen peroxide was obtained.

Mr. WYNNES inquired whether Professor Ramsay had examined the action of nitric oxide on nitric anhydride: it had been stated that the interaction was between N_2O_3 and N_2O_5 , but nitric oxide alone should have the same effect.

Professor RAMSAY, in reply, said that the method of preparing nitrogen peroxide described by Mr. Groves gave good results, but was less economical than his own. He had not examined the action of nitric oxide on nitric anhydride.

5. "Note on the Law of the Freezing-Points of Solutions." By S. U. PICKERING.

According to views explained in a previous communication (*Proc. Chem. Soc.*, 1889), the author considers the lowering of the freezing-point of a solvent to be attributable to three actions, which he distinguishes as mechanical, physical, and chemical. He has now succeeded in reducing the values for these actions into one equation, which gives the total lowering of the freezing-point, t° , to be—

$$t^{\circ} = \frac{K + 167 \pm \sqrt{(K - 167)^2 - 668 \frac{Kl + H}{Ac}}}{2},$$

where l is the heat capacity of the limiting hydrate (that is, the hydrate from which no amount of cooling could make water crystallise out); H the heat absorbed in the decomposition of the hydrate (or hydrates) constituting the solution taken into the next lower one; A the maximum number of water molecules which could be crystallised out by excessive cooling; C the heat capacity of water. The author applies a small correction to Person's so-called absolute zero, -160° , based on a combination of Person's with Regnault's values for the heat capacity of ice, and gets -167° , a value which he finds to give results in his calculations of the freezing-points agreeing with those found even more closely than -160° did. K represents the "mechanical" lowering, this being equal to—

$$\frac{n167m}{300},$$

in which n is the number of foreign (fundamental) molecules (of sulphuric acid in the case taken) to 100 H_2O , and m the number of fundamental molecules constituting the active molecule of the solvent; in the case of water, m is generally 3.

In his former communication the author stated that the triple molecules of water began to simplify when sulphuric acid solutions of 30 per cent strength were reached, being resolved into simple or H_2O molecules when the

strength reached about 38 per cent. The above equation shows that this simplification must occur. As the strength of the solution increases, K becomes bigger, and a point is reached where value of—

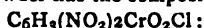
$$668 \frac{K+H}{Ac}$$

is bigger than $(K-167)^*$, so that the contents of the surd are negative, and there will be no freezing-point possible under these conditions. This occurs at 34 per cent: and the only way in which water could be frozen out of solutions of greater strength (as is the case) is by the reduction of the magnitude of K by the simplification of the $3H_2O$ molecules, that is, by the reduction of the value for m.

Proceeding with this reduced value for K, another point (37.95 per cent) is soon reached, where the freezing out of water would become impossible, even under these new conditions, and, as the H_2O molecules could simplify no further, it must cease absolutely: as a matter of fact it does so: the crystallisation of water ceasing at about 38.2 per cent, while that of the tetrahydrate begins.

6. "The Action of Chromium Oxychloride on Nitrobenzene." By G. G. HENDERSON, B.Sc., M.A., and J. M. CAMPBELL, B.Sc.

These substances interact, suddenly and with great violence, even at the ordinary temperature, and no definite products are obtained. When a 50 per cent solution of chromium oxychloride in dry chloroform is heated on the water-bath with a similar solution of nitrobenzene, hydrogen chloride is evolved and a brown powder slowly separates. After it has been washed with chloroform and dried, this powder has the composition—



it rapidly takes up moisture, and, when thrown into water, is decomposed with evolution of much heat, chromic chloride and chromic acid going into solution and nitrobenzene separating out, but the authors have failed to obtain the nitroquinone described by Etard. On using nitrobenzene containing nitrotoluene it was found, however, that a brown compound was produced which, when decomposed by water, gave nitrobenzene and, in smaller quantity, paranitrobenzoic acid; the latter substance has properties very similar to those attributed to nitroquinone, and it is suggested that Etard may have mistaken one for the other.

7. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 1. The Constitution of Betanaphthol- and Betanaphthylaminedisulphonic Acids, R and G Naphthalenedisulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNN.

The study of the tri-derivatives of naphthalene is of importance from many points of view, both technical and theoretical; several are largely used in the preparation of azo-dyes, and it is necessary that their constitution should be known in order that the dependence of colour and tinctorial properties on structure may be determined; and especially is this the case, as all are not equally valuable—betanaphtholdisulphonic acid G (Gelb), like the "Bayer" modification of betanaphtholmonosulphonic acid, interacting but slowly with diazo salts; while the corresponding betanaphthylaminedisulphonic acid, like the "Badische" modification of betanaphthylaminemonosulphonic acid, is incapable of forming azo-dyes.

Moreover, having characterised the dichloronaphthalenes by converting them into sulphonic acids, the authors were anxious also to determine the exact course of the change on sulphonation, especially as isomeric changes were noticed in several instances (*Proc. Chem. Soc.*, 1889, 52, 120), it being probable that much light would thus be thrown on the laws which govern substitution in the naphthalene series; and from this same point of view the comparative study of the influence exercised by radicles, such as Cl, OH, NH_2 , on the formation of disulphonic acids appeared likely to afford results of considerable interest.

In the case of the dichloronaphthalenes, which serve as reference compounds for di-derivatives of naphthalene, the author's previous work has shown how much has to be learnt by carefully characterising the several isomerides (*Proc. Chem. Soc.*, 1888, 704); and in the case of the trichloronaphthalenes, no fewer than fourteen of which are possible, which will ultimately serve as reference compounds for tri-derivatives of naphthalene, it is still more necessary to characterise each compound, owing to the close similarity which obtains between many of the isomerides; no fewer than four, for example, melt at nearly the same temperature, about 90–92°.

The study of the betanaphtholdisulphonic acids was commenced by one of the authors in 1880 (*Chem. Soc. Journ.*, 1881, 139). Results were obtained which led to the belief that both were derivatives of the Schaefer monosulphonic acid, but at that time no methods were available by which any final determination of their constitution could be effected. Subsequently attention was directed to the corresponding amido-disulphonic acids when these became procurable. About three years ago a liberal supply of the betanaphthylaminedisulphonic acid R, in the form of acid sodium salt, was obtained from the *Actiengesellschaft für Anilinfabrikation*, through the kindness of Dr. Martius. In the spring of 1888, the authors became aware of the results since published by Duisberg and Pfitzinger (*Ber.*, 1889, 396), and arranged with Dr. Duisberg to carry on the investigation.

Constitution of the Betanaphthylaminedisulphonic Acid R.—Duisberg and Pfitzinger inferred that this acid was derived from the α -naphthalenedisulphonic acid of Ebert and Merz, as the disulphonic acid obtained from it on displacing the NH_2 group by v. Baeyer's hydrazine process gave the dihydroxynaphthalene corresponding to the α -acid on fusion with potash. Although perfectly satisfied with this proof, the authors have thought it desirable to amplify the evidence in order to meet the possible objection that isomeric change may occur during the fusion, as in the case of benzene-derivatives. They find on directly comparing the disulphonic acid with the Ebert and Merz α -acid that the two behave alike; the sulphochloride derived from the amido-acid crystallising in large prisms which gradually become opaque, fusing at 158°, and yielding the dichloronaphthalene melting at 114° on distillation with PCl_5 .

By the Sandmeyer method the amido-acid may be converted into a chlorodisulphonic acid, the chloride of which crystallises in radicle groups of spear-like needles, melting at 165°; on distillation with PCl_5 this yields a corresponding trichloronaphthalene, which crystallises from alcohol in small spherical aggregates of minute scales or flat needles, melting at 90–91°.

Taking into account the previous determination of the constitution of the Ebert and Merz α -acid (*Proc. Chem. Soc.*, 1888, 48), the constitution of the amidodisulphonic acid R, and of the corresponding trichloronaphthalene is expressed by the formula:—

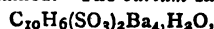


Betanaphthylaminedisulphonic acid R.

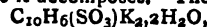


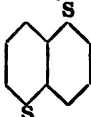
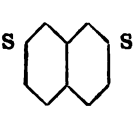
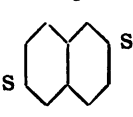
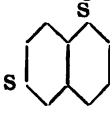
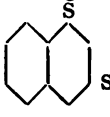
Trichloronaphthalene.
M. p. 90–91°.

Constitution of Betanaphthylaminedisulphonic Acid G.—A quantity of this acid was first procured from the *Actiengesellschaft für Anilinfabrikation*; we have to thank the *Farbenfabriken vormals, F. Bayer and Co.*, for a subsequent larger supply. On converting it into naphthalenedisulphonic acid by the hydrazine method, a new acid was obtained. The barium salt,—

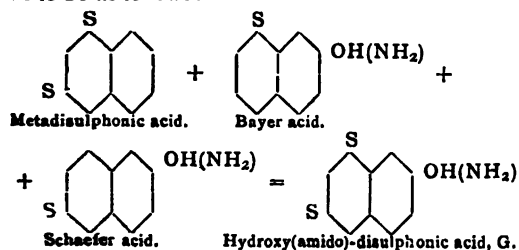


is very soluble in water, and has not been obtained in any definite crystalline form; it retains $1\frac{1}{2}H_2O$ at 270°, above which temperature it decomposes. The potassium salt,—

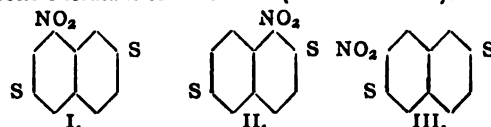


	1:4'	2:2'	2:3'	1:3'	1:3
					
(SO ₃ H) ₂ ..	Armstrong (<i>Chem. Soc. Journ.</i> , 1871, 173; <i>Ber.</i> , 1882, 205); Armstrong and Wynne (<i>Proc.</i> , 1886, 231; 1887, 42). Ewer and Pick, G. P. 41934.	Ebert and Merz (<i>Ber.</i> , 1876, 592).	Ebert and Merz (<i>Ber.</i> , 1876, 592).	Armstrong and Wynne (<i>Proc.</i> , 1886, 231); Armstrong (<i>Proc.</i> , 1889, 10). Ewer and Pick, G. P.	Armstrong and Wynne.
(SO ₃) ₂ Ba ..	+ 4H ₂ O, granules consisting of microscopic needles.	+ 2H ₂ O, long, broad needles.	+ H ₂ O, "crusts."	+ 4H ₂ O, granules consisting of microscopic needles.	+ 4H ₂ O, no definite form. Granular, very soluble.
(SO ₃ K) ₂ ..	+ 2H ₂ O, in prismatic needles.	+ 2H ₂ O, in needles.	Needles.	+ H ₂ O, granules, consisting of microscopic needles.	+ 2H ₂ O, small prismatic forms. Very soluble.
(SO ₃ Na) ₂ ..	+ 2H ₂ O, glistening scales.	+ 6H ₂ O, in lustrous needles.	+ H ₂ O, crystalline aggregates.	+ 7H ₂ O, long, broad needles.	Very soluble in water.
(SO ₃ Cl) ₂ ..	Needles which become opaque. M. p. = 183°.	Prisms which become opaque. M. p. = 158°.	Needles. M. p. = 216°.	Aggregates of small needles. M. p. = 127°.	Prisms or prismatic needles. M. p. = 137°.
Cl ₂ ..	Needles. M. p. = 107°.	Scales. M. p. = 114°.	Flat needles. M. p. = 136°.	Needles. M. p. = 48°.	Needles. M. p. = 61.5°.

is very soluble, but crystallises well in small prisms. The sodium salt is very soluble, and has not been obtained in a form fit for analysis. The chloride, C₁₀H₆(SO₂Cl)₂, crystallises from benzene in prisms, from acetic acid in prismatic needles, and from petroleum spirit in small needles; it melts at 147°, and on distillation with PCl₅ yield a dichloronaphthalene melting at 61.5°, convertible by sulphonation, &c., into a sulphochloride melting at 147°. The acid is therefore the metadisulphonic acid of naphthalene. The relative position of the sulphonic radicles being thus determined, their position relatively to the β-NH₂ radicle may be inferred from the facts that the hydroxy-G-acid is obtained as direct sulphonation-product of the Bayer modification of betanaphtholsulphonic acid, and that it yields the isomeric Schaefer acid when reduced by sodium amalgam. The authors first became acquainted with the latter fact from Dr. Caro, and have verified it in the course of an experimental examination of the behaviour of substituted naphthalenesulphonic acids generally on reduction; the details of this work will be given later on, but it may be here stated that, although the sulphonic acids are usually reducible to naphthalene in the manner first pointed out by Otto in the case of naphthalene-α-sulphonic acid, the β-sulphonic derivatives are far less readily affected; the NH₂ radicle also exercises a special protecting influence in many cases. Superposing the various results, the constitution of the G-acid is shown to be as follows:—



The G-acid is convertible by Sandmeyer's method into a chlorodisulphonic acid, the chloride of which crystallises from benzene in long radiate needles, melting at 170°; this is converted by PCl₅ into a trichloronaphthalene which crystallises in very slender needles, melting at 113°, identical with that obtained by Alén (*Ber. Referate*, 1884, 437) from an α-nitro acid prepared by nitrating the β-disulphonic acid of Ebert and Merz. This result confirms the conclusion above arrived at, as of the three possible formulæ of Alén's acid (see Table above).



II. and III. are excluded by the fact that the trichloronaphthalene corresponding to III. melts at 90–91° (*vide supra*), and that corresponding to II. also at about the same temperature (*cf. Proc. Chem. Soc.*, 1889, 52).

The results now obtained show that, as in the case of the Bayer and Badische monosulphonic acids, the action of diazo-salts on the G-disulphonic acids is either retarded or prevented by the "protecting influence" exercised by an α-1'-sulphonic group.

The properties of the five known naphthalene-disulphonic acids are summarised in the appended Table.

The authors wish it to be understood that they *entirely reserve* the investigation of the metadisulphonic acid and of its derivatives; this being the third acid of the series of which they have first investigated the preparation and properties, they believe they are justified in claiming this privilege.

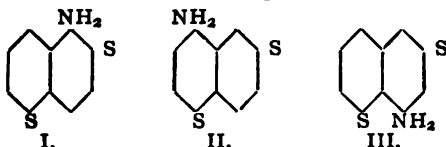
8. "Studies on the Constitution of Tri-derivatives of Naphthalene. No. 2, α-Amido 1:3'-Naphthalene-disulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

The 1:3'-naphthalene-αβ-disulphonic acid first described by the authors in 1886 (*Proc. Chem. Soc.*, 1886,

231; 1889, 10) has recently acquired considerable technical importance on account of the peculiar behaviour of the amido- and corresponding hydroxy-acid prepared from it, and as the source of valuable dye-stuffs (cf. Bernthsen, *Ber.*, 1889, 3327). This amido-acid has been patented by the Actiengesellschaft für Anilinfabrikation, in whose laboratory it was first prepared, by M. Andresen (cf. Schultz, *Ber.*, 1890, 77), by nitrating our acid, and reducing the nitro-derivative. We were naturally interested in determining the constitution of the amido-acid, and soon after it became known were favoured with a supply of material by the Actiengesellschaft für Anilinfabrikation. Technically, it has become known as α -naphthylamine- α -disulphonic acid; but it appears very undesirable to perpetuate the confusion in nomenclature which reigns supreme in the case of the α -naphthylamine acids by adopting and continuing this name. We first satisfied ourselves that the amido-acid had been prepared from our $\alpha\beta$ -disulphonic acid by reducing it by the hydrazine method; the acid obtained gave a sulphochloride melting at 127°, and a dichloronaphthalene melting at 48°.

The corresponding chlorodisulphonic acid was then prepared by Sandmeyer's method; the disulphochloride of this acid crystallises from petroleum spirit in tufts of very slender needles, melting at 110°; on distillation with PCl_5 , it is converted into a trichloronaphthalene, which appears to be dimorphous, crystallising from alcohol either in long slender needles, melting at 87°, or in large flat prisms, melting at 90°.

As the amido-acid is known to yield α -naphthylamine when deprived of its sulphonic groups, there are only three formulæ which can be assigned to it:—



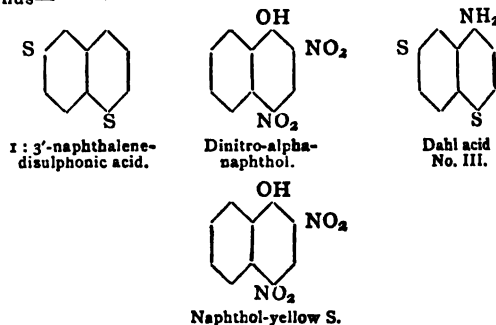
Formula I. is precluded, as the corresponding trichloronaphthalene melts at 78° (*Proc. Chem. Soc.*, 1889, 49); formula II. is likewise precluded, as the corresponding trichloronaphthalene (*vide infra*) melts at 65° and 56°; formula III. therefore expresses the constitution of the acid. This result confirms, and is confirmed by, the conclusions arrived at by Bernthsen, who finds that the corresponding hydroxy-acid exhibits the behaviour of the 1:1'-hydroxy-sulphonic acid, readily yielding a naphthalene-sulphonolactone-sulphonic acid. Although slightly longer than the name proposed by Bernthsen, this latter appears to us to be preferable. The present tendency to construct a name on rational principles, so as to express the nature of the substance designated, and then to deprive it of all meaning by elision of the significant syllable, is most irrational; the term *sulphonolactone* is expressive, and not inelegant; sultone conveys no meaning to the un instructed ear.

9. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 3. Alphanaphthylaminedisulphonic Acid, Dahl, No. III. The Constitution of Naphthol-Yellow S." By HENRY E. ARMSTRONG and W. P. WYNNE.

It is well known that when alphanaphthol is sulphonated by excess of sulphuric acid, it is readily converted into acids capable of yielding naphthol-yellow S, a most valuable dye-stuff, the sulphonic acid of dinitroalphanaphthol, on treatment with nitric acid; although it is known that the yellow is a heteronuclear derivative, and that the sulphonic group is in $\alpha\beta$ -position, inasmuch as it yields 1:2:4-sulphophthalic acid on oxidation (cf. Græbe and Rée, *Chem. Soc. Trans.*, 1886, 522), the position of this group has not hitherto been determined. With the object of ascertaining the constitution of the yellow, the authors have examined the alphanaphthyl-

aminedisulphonic acid No. III. prepared by sulphonating naphthionic acid with 35 per cent anhydrosulphuric acid at a temperature not exceeding 30°, described in the German patent, No. 41,957, 1886, of Dahl and Co., this acid being very readily converted into the yellow by diazotising, and then heating with nitric acid. Through the kindness of Dr. Caro, a considerable quantity of this acid was obtained from the Badische Anilin und Soda-fabrik.

When reduced by the hydrazine method, the Dahl No. III. acid is found to yield the author's 1:3'-naphthalene-disulphonic acid; the sulphochloride actually prepared from the acid, melted at 127°, and the corresponding dichloronaphthalene at 49°. Taking into account the fact that naphthol-yellow S is a heteronuclear β -sulphonic derivative, this result is alone insufficient to determine the constitution of the yellow and of the amido-acid, thus—



The chlorodisulphonic acid prepared from the Dahl acid yields a sulphochloride very soluble in benzene, from which it crystallises in small prisms; it separates from petroleum spirit in rosettes of small apparently rectangular prisms, melting at 107°. The corresponding trichloronaphthalene affords a remarkable case of dimorphism; it is sparingly soluble in hot alcohol, from which it crystallises in slender needles melting at 65°; if the melting-point be re-determined as soon as solidification has taken place, it is found to be 56°, but if determined after a longer interval 65°, as in the first instance. This trichloronaphthalene should be identical with that prepared by Widman from dichloronaphthalene- β -sulphonic chloride, which the authors have shown to be a derivative of 1:4-dichloronaphthalene (cf. *Proc. Chem. Soc.*, 1888, 106), but Widman's product is said to melt at 56°; the authors find, however, on preparing it according to Widman's direction, that it also melts at 65° or 56°. By nitrating 1:3'- γ -dichloronaphthalene Clève obtained a nitrodichloronaphthalene yielding a trichloronaphthalene melting at 65°; the author's observations show that this is in reality identical with the Widman trichloronaphthalene, and therefore that the behaviour of 1:3'-dichloronaphthalene on nitration is perfectly "normal," and strictly comparable with that of both α - and β -monochloronaphthalene.

By sulphonating 1:4-chloronaphthalenesulphonic acid in the form of potassium salt by means of the theoretical proportion of sulphuric anhydride employed as 20 per cent anhydrosulphuric acid at 100°, the authors have obtained a chlorodisulphonic acid identical with that prepared from the Dahl amido-acid; showing that the α -chloro, α -amido, and α -hydroxy-monosulphonic compounds behave similarly on further sulphonation; but it remains to be ascertained whether the series of changes leading up to the production of the final stable compounds is identical in the several cases.

The Oxides of Manganese.—Alex. Gorgen.—The wads of psilomelanes are true acid hydrated manganites, the most characteristic samples of which have the composition $3(\text{MnO}_2)\text{RO} + 1$ to 3HO .—*Comp. Rend.*, No. 5.

NOTICES OF BOOKS.

Warren's Table and Formula Book; containing, in addition to the usual Tables, an Account of some Physical Electrical Units now in use among Scientific Men, Important Formulæ in Algebra, Mensuration, and Trigonometry, together with Valuable Information on Transactions in Exchange and Commerce. By the REV. ISAAC WARREN, M.A. London: Longmans, Green, and Co.

THIS collection of tables and formulæ will be exceedingly useful to students of physics, the more so as the figures given are exceptionally correct.

We notice one only typographical error, to wit, the German mark is, on p. 119, said to be " $=100$ groschen $=100$ pfennige," thus making the groschen and the pfennig equal to each other. It should, of course, have been said " $=10$ groschen."

The tables of British weights and measures remind us of the number of different local standards, which even the introduction of the metric system would not do away with unless accompanied by most drastic legislation and equally drastic espionage. Thus, in this work and in actual practice in the South of England the gill is synonymous with the noggin, and is $\frac{1}{2}$ pint or 5 fluid ounces. But in the northern counties the gill $=\frac{1}{4}$ pint, or 10 fluid ounces, and is double the noggin. The difference between Irish and statute acres is duly mentioned, but it might have been useful to add the dimensions respectively of the Lancashire and the Cheshire acre, which are both larger than the Imperial standard. In some parts of Yorkshire the acre is dispensed with altogether, and land for selling or letting is stated as so many "days' work."

Many mineral-brokers have the vicious custom of expressing any fractions of a per cent of valuable matter in "eights." Thus, instead of saying that a copper ore contains 5.75 of copper, they will call it 5 $\frac{3}{4}$ ths. Here, also, belongs the custom of assigning to sodium, not its true atomic weight, but a false and arbitrary number. This custom occasionally involves analysts in unedifying disputes.

A further element of confusion is the fact that the American quart is rather smaller than the litre, whilst the British legal quart is larger.

The author remarks that though the General Medical Council directed the disuse of the drachm and the scruple in medical prescriptions, yet physicians persist in their use. It is not even certain whether these denominations are to refer to the old Troy ounce or the new Avoirdupois ounce.

If the introduction of the metric system would sweep away all the above-mentioned anomalies, it would be welcome; but if it merely co-exists with our ancient denominations, its avatar would render confusion worse confounded.

CORRESPONDENCE.

BRIN'S OXYGEN COMPANY.

To the Editor of the Chemical News.

SIR,—A good deal of unnecessary alarm has been caused by the lamentable accident which occurred rather more than a week ago at Glasgow through the bursting of a cylinder. There is no occasion either for alarm or surprise when the facts of the case are known. If we hear of a man who deliberately throws a lighted match into a barrel of gunpowder, we are neither alarmed nor surprised at the results. This is exactly what has occurred at Glasgow. The unfortunate man who lost his life charged hydrogen into a black cylinder (in direct contravention of the Company's rules), and afterwards, for

getting that he had done so, put oxygen into the same vessel; the result was an explosion, which took place at the first slight concussion which the cylinder received. A piece of the cylinder which was picked up four yards from where the accident occurred was quite hot, showing conclusively that ignition had taken place, and there could have been no spontaneous ignition if the two gases had not been present.

Every precaution is taken by the Companies to prevent the possibility of O and H getting mixed; under no circumstances will they fill hydrogen or coal-gas into a black cylinder, or oxygen into a red one; neither will they put the one gas into a cylinder which they even suspect has ever contained the other.

With a view, however, of making it absolutely impossible for two gases to be put in the same cylinder, it has been decided by this company, and also by the Scotch and Irish Oxygen Co., and the Manchester Oxygen Co., to fit all hydrogen cylinders with a left hand thread, so that they cannot be filled at the oxygen pump, and, in the same way, it will be impossible to fill oxygen cylinders at the hydrogen pump. All consumers are earnestly requested to send their hydrogen cylinders either to the Companies or to the agents through whom they obtain their supplies of gas, to have the alteration made, and the smallest possible charge will be made for taking off the present valves and fitting on new ones. After a certain limit of time, of which notice will be given, no hydrogen or coal-gas cylinders not provided with the new thread will be filled.

In some quarters, the fear has been expressed that the accident at Glasgow occurred through over-pressure; any such apprehension may be immediately dismissed from the mind; explosion from such a cause is impossible; the cylinders are tested to double the pressure at which they are ever filled, and it is impossible to exceed the standard filling pressure of 120 atmospheres. They are also re-tested periodically. For years past, the Government have been using high-pressure cylinders for ballooning purposes, similar to those in use at present; they had them in the Egyptian and Boer campaigns, and they have frequently been rolled from the top of a hill to the bottom, bounding from point to point, and in no single instance has an accident occurred or a cylinder burst.

In conclusion, I would remind you of the fact that since oxygen and hydrogen have been supplied in high-pressure cylinders—now some three or four years—only two accidents have occurred, and these at the works; whereas, when bags were in vogue, accidents, in many cases fatal, frequently took place. Only last week, in America, a lecturer on chemistry and ten or twelve of his pupils were seriously injured by the bursting of a retort in which oxygen was being made by the old-fashioned chlorate of potash process.—I am, &c.,

T. HESTER,

Secretary to Brin's Oxygen Co. (Lim.).

Brin's Oxygen Company (Lim.),
Connaught Mansions, Victoria Street,
Westminster, S.W., Feb. 7, 1890.

THE IGNITING-POINT OF SULPHUR.

To the Editor of the Chemical News.

SIR,—The letter from Mr. Blount (CHEM. NEWS, vol. lxi., p. 85) about the igniting-point of sulphur is of considerable interest to those chemists who have to do with explosives, either technically or as teachers. When one comes to think about it, a substance "should" have a fixed igniting-point. But almost all substances show great variations in this respect, and whether these are due to physical state, as with charcoal and diamond, or merely mechanical sub-division, has not been very closely enquired into.

I am certainly inclined to the belief that the igniting-point is determined solely by the physical or allotropic state of the body, in cases like carbon and silicon. In the case of substances like sulphur, which volatilise, the igniting-point must be above the boiling-point.

Experiments with iron reduced by hydrogen, and lead reduced from tartrate, are often shown as instances of the low temperature at which these substances "ignite," . . . but do they really ignite at a lower temperature? To get lead to burn in air requires a pretty strong red heat, say, 700° C. If the lead powder from tartrate be put carefully on to the flattened bulb of an air thermometer, a steady rise of temperature will be noticed until the mass glows, by which I understand the igniting-point, similarly with iron, only the rise is more rapid; the small particles oxidise and the temperature rises locally to that of ignition.

In the case of sulphur the allotropic condition can have no, or but little, effect, for the substance, I believe, only ignites after it has attained the gaseous state. I have not attempted the matter in any strict way but for lecture purposes. As is well known, sulphur boils at 448° C., and the vapour may escape into air, as in distilling it, without ignition taking place. I have arranged a wide tube, a lamp cylinder, horizontally about half an inch above an iron plate heated by a large burner to something above the melting-point of zinc—415°; into this tube, when heated, I distil a few drops of sulphur at about the middle; it vaporises, and, of course, comes in contact with hot air at the two ends, but I have not found any time that ignition took place when the plate was just hot enough to melt zinc foil. I have not yet ventured to risk a nitrogen thermometer in the tube itself.

That sulphur ignites in air at any temperature below 300° C. I think quite out of the question. Nitre melts at 330° C., and sulphur may be put on to this, when it melts, and, of course, goes very dark in colour, and with little care, most, if not all, may be sublimed from the nitre before any chemical action takes place. Sulphur dropped on to fused potassium chlorate certainly burns at once, but the melting-point of KClO_3 may be higher than that of nitre. However this point may be determined, it will, I think, be found to be above the boiling-point.

It must also have happened to scores of people to notice that boiling sulphur can be poured through air into water, in the usual experiment of making the elastic variety, without ignition taking place. The thin stream of sulphur in this case cannot be much below the temperature of boiling (448°).

Probably the mistakes about the ignition-point of sulphur have arisen from neglect of the fact that it is one of the worst conductors of heat. When put in a flame, a piece of sulphur takes fire rapidly, because it becomes locally heated up to above its boiling-point; it always melts before igniting. A moderate sized sulphur flame will deposit sulphur on a cold object held in it.—I am, &c.,

W. R. HODGKINSON.

Woolwich, Feb. 15, 1890.

OCCURRENCE OF PHOSPHATES.

To the Editor of the Chemical News.

SIR,—All kinds of strange hypotheses have been advanced to account for the irregularity and fortuitous manner in which calcic phosphate occurs in various formations. Two facts can hardly fail at once to strike anyone as to these deposits:—(1) The irregularity of their occurrence. (2) Their superficial nature. I have had the good fortune to visit pretty many of these at different times, and the addition of one more to the various more or less impossible theories which have been formed as to their origin (none of these accounting for the peculiar conditions in which they are found) can hardly do any harm. I would suggest, then, that in many cases these formations may have had their origin in the constitution of

colonies of infusoria or marine insects which would have been more likely to have existed in the quiet recesses of caves and clefts of the rocks, where phosphates so often are found. We must presume that the bodies of many infusoria are largely composed of calcic or other phosphates, to judge from the wonderful manner in which their propagation is assisted by the presence of compounds rich in phosphoric acid, and we know also the manner in which they can gather and assimilate to themselves the materials necessary to their existence. Phosphates seem to be distributed, though often in small quantity, throughout the entire crust of the earth, and so they might be brought in a state of solution to the infusoria, which would thus gradually attract to themselves the phosphates they required, especially those in their more immediate neighbourhood. Fish in search of food would be attracted by the organic life of these colonies, and dying, their bones and debris and those of the predatory fishes following them would notably augment the deposits. Such a theory, if true, would, in a great measure, account for the superficial nature of most of these deposits and for their comparative purity, as well as for the poverty in phosphates often observable in the surrounding strata. It would also afford some explanation why phosphates are so often placed in holes and cavities of the rocks, instead of forming continuous veins, like other minerals, and it would afford some reason for the mixed nature of these deposits, which, so far as the more modern ones are concerned, are generally composed of pulverulent matter more or less agglomerated together, interspersed with the teeth and bones of fishes, the organised structure of which is still often apparent.—I am, &c.,

F. MAXWELL LYTE.

LARD.

To the Editor of the Chemical News.

SIR,—I have read the letter of Mr. Swindells, Ph.D., which appeared in the *CHEMICAL NEWS*, vol. lxi., p. 85. I know nothing about tea, therefore I am unable to speak about that subject; but having, for many years, been connected with the refining and canning of American lard, between three and four thousand tons of that commodity having annually passed under my supervision, I think you will concur with me that I ought to be able to express a pretty correct opinion as to the general purity of refined lard. Mr. Swindells says "he can believe anything of this commodity." I decline to be so credulous, or to surround any article of food with unnecessary doubt and distrust as to its purity. The public, as a rule, insist upon having pure and wholesome articles of food, and Parliament enacts laws to punish those that do not supply such. So far I am satisfied. The only difficulty which arises in my mind with respect to American lard is the soft condition in which it arrives in this country, especially in the summer. This condition is mainly owing to the small quantity of stearin found in the fat of the common hog. Ox fat, like hog's lard, is a mixture of stearin, margarin, and olein, but contains more stearin than hog's lard. The fat of oxen, since it has been used for the manufacture of oleomargarin (now so extensively used in the preparation of artificial butter), is rendered down while perfectly fresh and sweet, the residual stearin being as good for food as its other constituents. As I have intimated, steam granulated lard is a soft and sloppy article, and could not be transmitted by rail in open packages. In order to so transmit it, it has to be made more dense. Stearin is the hard constituent of all fats, and I can see no reason whatever, either on the ground of purity or economy, that ox stearin should not be mingled with lard, for they are both legitimate and wholesome articles of food; and, in my opinion, the stearin of the ox is much superior, as regards quality and freshness, to that obtained from hog's lard. I am not

singular in this opinion, as it has already been advanced by some distinguished chemists and physicists of the Victorian age. With respect to the use of cotton-seed oil as an adulterant of lard, it is well known that such a mixture must be sold as a compound. I will not enter upon its merits. No refiner dare incorporate 20 per cent of water with lard without selling it as watered lard. But the watering of lard is, I think, now almost defunct. The steam-rendered lard of the Western States arrives in Liverpool to-day as pure as ever it arrived. Of course, now and again, inferior parcels come to hand; and this must of necessity be so, seeing that the hogs are fed in some districts on corn, in other districts in forests, and in other places on distillery refuse. In the English refineries the firm and corn-fed lard is mingled with the soft and flabby article, and then cleansed and refined. The operations carried on in the refineries are on so extensive a scale, that anything savouring of "mystery" would only result in ruin and disaster to those who did the wrong.

With respect to the addition of other matter to lard, I presume Mr. Swindells alludes to stearin. Now, as stearin is a constituent of lard, and is refined with it, its use, I should say, will bring it under the 6th Section of the Sale of Food and Drugs Act, which provides that an offence shall not be deemed to be committed "Where any matter or ingredient not injurious to health has been added to the food or drug because the same is required for the production or preparation thereof as an article of commerce in a state fit for carriage or consumption, and not fraudulently to increase the bulk, weight, or measure of the food or drug or conceal the inferior quality thereof."

This section might have been specially drafted for this particular addition.—I am, &c.,

WILLIAM BROWN.

3, Hereford Road, Seaforth,
Liverpool, Feb. 18, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

OTA.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 4, January 27, 1890.

The Substitution of Salts in Mixed Solutions.—A. Etard.—This paper cannot be intelligibly abstracted without the use of the accompanying diagrams.

The State of Iodine in Solution.—Henri Gautier and Georges Charpy.—The solutions of iodine are divided into two classes; the brown solutions (alcohol, ether, &c.) and the violet solutions (carbon disulphide, chloroform, benzene, &c.). The authors have treated iodine with fifteen solvents, and they arrange the colours in a series from violet to brown. The absorption-spectra of the solutions vary also in a continuous manner. In the violet solutions they show a spectrum approaching that of the vapour of iodine, but the dark band begins, not in the red, but in the yellow, and encroaches a little more upon the blue than in the vapour of iodine. In the succeeding groups the displacement of the dark band on the side of the violet is intensified. The authors conclude that the mol. of iodine which, in the brown solutions, corresponds to I_2 , is gradually split up so as to approximate to I , which corresponds to iodine in the state of vapour. This hypothesis appears to be supported by the influence exerted by temperature upon the colour of the solutions.

Calorimetric State of the Sodium Phosphites and Pyrophosphites.—L. Amat.—Not capable of abstraction.

Action of Ethylmalonyl Chloride upon Ethylbenzene in Presence of Aluminium Chloride.—A. Béhal and V. Auger.—The product obtained is metadiethylbenzene, of the sp. gr. (at 0°) 0.8812. Its refraction index at $14^\circ = 1.472$.

No. 5, February 3, 1890.

Combinations of Gaseous Ammonia and of Hydrogen Phosphide with Silicon Dichloride and Dibromide.—M. Besson.—The author has verified the composition of the ammonium compound, $Si_2Cl_6NH_3$, as given by Persoz. The composition of the bromide is different, $Si_2Br_4.7NH_3$. The latter is a white amorphous solid, similar to the corresponding chloride. It is decomposed by water, and yields a strongly alkaline liquid which gives off ammonia. Hydrogen phosphide has no action upon silicon dichloride, except the latter is cooled down to -23° , when it absorbs 23 vols. of hydrogen phosphide, and at -50° to -60° , 40 vols., forming a liquid of the composition $Si_2Cl_4.2PH_3$. A crystalline compound is obtained by the joint action of pressure and refrigeration.

Part played by certain Foreign Bodies in Iron and Steels.—F. Osmond.—During the slow refrigeration of an electrolytic iron containing 0.08 per cent of carbon there ensue two liberations of heat; the one which the author calls a_3 causes the thermometer to be stationary at 855° ; the other at a_2 , less marked, presents its maximum about 730° . The bodies whose influence has been specially examined are boron, nickel, copper, silicon, arsenic, and tungsten. Boron acts in a manner analogous to carbon; a_3 is lowered in part to between 815° — 805° , and in part to 735° — 725° . In a steel free from nickel a_3 and a_2 are blended together, but a_1 (the tempering heat of steel) remains distinct. The presence of nickel brings a_3 , a_2 , and a_1 into a single point together between 660° and 640° . The action of copper on the allotropic transformation of iron is analogous to that of carbon, but less energetic. Silicon prevents the allotropic transformation. Arsenic acts similarly to silicon. Tungsten has a doubtful influence, but it lowers a_1 to 540° — 530° .

Journal für Praktische Chemie.

New Series, Vol. xl., Nos. 18 and 19.

The Oxygen Acids of Iodine.—C. W. Blomstrand.—An account of iodic acid and its double acids with other acids, such as iodosulphuric acid, molybdosulphuric acid, with its potassium, ammonium, thallium, and lead salts, iodonitric acid, iodochromic acid, and the acid alkaline iodates.

Thermo-chemical Researches.—F. Stohmann, Cl. Kleber, and H. Langbein.—This paper is incapable of useful abstraction.

Action of Alkalies and Ammonia upon the Haloid Substitution-Products of the Quinones.—Fr. Kehrman.—A study of the action of potassium ethylate upon chloranil; that of iodethyl upon silver chloranilate; the behaviour of iodmethyl with silver chloranilate and the conversion of the β -isomers into the α isomers.

Researches from the Laboratory of the University of Freiburg.—These comprise memoirs by Ad. Claus and C. Geissler on the dibromquinolines; by Ad. Claus and G. N. Vis on orthometadibromquinolines and certain derivatives of metabromquinoline and of anabromquinoline; and Ad. Claus and Ad. Weiter on bromised derivatives of quinoline.

Researches from the Laboratory of Prof. Alex. Saytzeff at Kasan.—Consisting of researches by Serg. Reformatzky on the synthesis of glycerins by means of hypochlorous acid.

Reply to the Answer of K. Hazura, and "Putting Matters Right."—K. Peters.—Two controversial papers, both relating to a memoir by A. Saytzeff on the oxidation of oleic acid with potassium permanganate.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Wool.—Could you, through the columns of the *CHEMICAL NEWS*, state the specific heat of wool, or mention where I could get the desired information.—*ENQUIRER*.

MEETINGS FOR THE WEEK.

- MONDAY, 24th.**—Medical, 8.30.
Society of Arts, 8. "Stereotyping," by Thomas Bolas, F.C.S.
- TUESDAY, 25th.**—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
- WEDNESDAY, 26th.**—Society of Arts, 8. "The English in Florida," by Arthur Montefiore.
Geological, 8.
- THURSDAY, 27th.**—Royal, 4.30.
Institute of Electrical Engineers, 8.
Royal Institution, 3. "The Three Stages of Shakespeare's Art," by Rev. Canon Ainger, M.A., LL.D.
Chemical, 5. "The Northern Shan States and the Burma-China Railway," by William Sherriff.
- FRIDAY, 28th.**—Royal Institution, 9. "Evolution in Music," by Prof. C. Hubert H. Parry, Mus. Doc. M.A.
Quekett Club, 8. (Anniversary).
- SATURDAY, March 1st.**—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.

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C. CROWTHER SMITH, Secretary.

Ogle Road, Southampton,

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See opinion *Electrical Review*, October 21.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1579.

A PROCESS FOR DECOMPOSING COMMERCIAL NICKEL AND ITS SALTS AND GALVANICALLY COATING OBJECTS WITH PURE NICKEL.*

I, GERHARD KRÜSS, Lecturer at the University of Munich, Doctor of Philosophy, of Munich, in the Empire of Germany, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

According to experiments, made by the inventor, metallic nickel, regardless of the known technical impurities contained therein, for instance, iron, copper, arsenic, manganese, silicon, &c., is not a chemical element, but an alloy. This alloy contains averagely about 98 per cent of a metal, similar indeed in its properties to the substance hitherto named "nickel," but finer in various respects, which metal I will designate with "Ni," and about 2 per cent of an element considerably differing from nickel in its properties and in the nature of its compounds. This element shall for the present be designated with "X."

Ni, free from X, that is to say, nickel in the new sense of the word, is produced from common nickel, nickel salts, or direct from the solutions of the raw materials obtained by concentration smelting, by proceeding according to the different nature of these elements. It is impossible to separate pure Ni by one operation from the said alloy of Ni and X, very rich in Ni, as the combinations of X, also if insoluble in the residue of their precipitant, are soluble in Ni-salts, therefore resist separation from the latter. It is therefore necessary to repeat one of the hereafter mentioned operations several times, or preferably several of these operations are successively performed to obtain pure nickel. Said operations are derived from the following peculiar properties of the compounds of the element X.

The neutral chloride, which is colourless—

(1) When treated with concentrated alkali lyes or melted with caustic alkali, is not changed into a hydroxide insoluble in water, but any hydroxide produced is wholly or partly converted into a combination of alkali soluble in water. The snow-white hydroxide precipitated by means of common alkali lyes, for instance $\frac{1}{2}$ normal solution, is, however, very little soluble in the latter, also with the addition of a large residue of the precipitant.

(2) Is but incompletely precipitated in solution through oxalic acid at a low as well as at a high temperature, more completely, however, through oxalate of ammonium even at a low temperature after short standing. A very great residue of the latter precipitant can return the precipitant into solution.

(3) Is not precipitated in solution through fixed alkali lyes or ammonia, oxalate of ammonium or oxalic acid, even at a high temperature, if the solution has been previously acidified by the addition of organic acids, for instance, acetic acid, citric acid, pyrotartaric acid, &c.; whereas the soluble double oxalates of Ni are decomposed, on heating their solution, by one of the said acids, and deposit insoluble oxalate of nickel. If the combinations of the element X are, in solution or otherwise, brought in contact with a metal which is more electro-positive than Ni, for instance, with zinc, the compounds are not reduced even by short heating.

All these properties inherent on the pure X-compounds are to a different extent or completely altered and concealed if a solution contains besides X-salts also combinations of Ni. This is the case in the nickel salt solutions of former designation. The white hydroxide of X, for instance, is not at all precipitated by ammonia, if, in a nickel salt solution of former designation, more than 70 per cent of the dissolved substance consists of Ni salt.

If the nickel raw materials obtained by concentration smelting contain mixtures, rich in X, of Ni and X, or of their salts, or solutions rich in X, of commercial nickel or commercial nickel salts, the neutral solutions, to separate the Ni from the X, are mixed with ammoniacal oxalate of ammonium, till the precipitate produced is re-dissolved. Subsequently they are allowed to stand for some time, white basic oxalate of X being thereby precipitated, and some more ammoniacal oxalate of ammonium is added. This addition is repeated until, after some longer standing, the quantity of the white precipitate ceases to increase. The blue liquid above the precipitate having been evaporated, its residue is thoroughly glowd and then mixed with such a quantity of muriatic acid as is required for solution. The solution of chloride is subsequently concentrated, and while heating it, solid hydrate of soda, up to five times the weight of the chloride, is incorporated therein, the doughy mass thereby produced being kept melting for a short time. The molten mass when cooled is broken up and brought in small pieces into ice-cold water, care being taken, if necessary by the addition of ice, to prevent the temperature of the liquid from rising above 10° C. Thereby the sodium compound of the oxide of X is dissolved, while rather pure hydroxide of Ni remains undissolved. The alkaline liquid containing X having been poured or drawn off after some standing, the hydroxide of Ni is washed by decantation and dissolved in weak mineral acids or in acetic acid. This solution is mixed with such organic acids as are also capable of preventing the aluminium from being precipitated through alkalis, for instance, with acetic acid, pyrotartaric acid, or citric acid. On adding soda lye to the liquid thus obtained, while heating, pure hydroxide of Ni, free from X, is precipitated; or pure oxalate of Ni, free from X, can be produced in boiling heat by precipitating the said solution of nickel, acidified with an organic acid, with soluble oxalates, for instance, oxalate of ammonium, all X being thus kept in solution, as by the preceding operations the greater part of X has already been eliminated from the commercial nickel or its salts.

In lieu of this, however, also the solutions of commercial nickel, of its salts, or of the nickel raw materials obtained by concentration smelting, and the nickel compounds produced by the above treatment may be decomposed into pure nickel (Ni) or its salts and the element X or its compounds respectively, by bringing the nickel compounds or solutions referred to in contact with a metal which is more electro-positive than the Ni-metal itself.

Nickel salts are in this manner more easily reducible, and, for instance, a solution of sulphate of nickel, chloride of nickel, or nitrate of nickel is soon almost completely decoloured when warming it with zinc dust or fine zinc chips, nickel metal being precipitated and zinc brought in solution as sulphate. The compounds of X are thus not reduced and remain in solution.

If the neutral or weak acid solutions of the nickel raw materials, obtained by concentration smelting, or like solutions of commercial nickel or nickel salts contain but few X-compounds, pure nickel can be obtained from them by performing once or twice one of the two last described operations.

The pure nickel obtained by the above described process is particularly adapted for galvanically coating objects. While the nickel obtained by the processes already known has a brownish yellowish hue, owing to the metal heretofore named X, inherent thereto, the colour of pure nickel (Ni), if not perfectly free from a yellowish shade, is decidedly more like silver and lighter, its application

* Complete Specification of a Patent granted to Gerhard Krüss, A.D. 1889, 25th January. No. 1428.

consequently preferable to the galvanic nickeling heretofore in use. To this end, any of the known processes may be applied by using nickel salts free from X for producing the alkaline neutral or acid nickel baths, and as nickel anodes such of nickel free from the element X, or from its oxide.

Having now particularly described and ascertained the nature of this invention, and in what manner the same is to be performed, I declare that what I claim is—

(1) The process for decomposing commercial nickel and its salts into pure nickel (Ni) or into pure nickel salts and into an element, designated with "X" in the specification, or its salts, that is to say, the process for producing such metals (Ni and X) and their compounds, substantially as described.

(2) The application of nickel, free from the element designated with X in the specification, or of the salts of such nickel for galvanically coating objects.

GERHARD KRÜSS.

Dated this 25th day of January, 1889.

A BRIEF SUMMARY ON PRACTICAL MANIPULATION.

By H. N. WARREN, Research Analyst.

(Concluded from p. 63).

Disintegration.

THE pulverisation of many substances, before operating further upon the same, not unfrequently presents one of the most irksome and troublesome undertakings that are to be met with in a laboratory, especially when adopting the general method of pestle and mortar. Quite recently small disintegrators have been supplied for practical purposes; but the present costliness of the article considerably retards their general application. In cases where it is required to reduce to powder, such as, for instance, the pulverisation of minerals, several pounds may be quickly reduced to any mesh by the application of a smooth iron plate, replacing for a pestle a large flat-headed hammer, and giving to the same a rotary motion, so as to constantly bring the same particles under its influence.

Casting and Moulding.

After the assay of a metal has been completed, it not unfrequently happens that a sample of the same is required in an elongated form in order to examine its tensile strength or other physical features. A very ready mould, and one which answers the purpose admirably on account of the non-introduction of foreign substances, may be formed by coiling round an ordinary pencil, or other convenient appendage, several thicknesses of writing-paper, closing the extremity by means of a cork, and supporting the same by immersing it to the extremity into dry sand, afterwards withdrawing the core and pouring into it the intended metal. A very perfect and uniform cast is thus obtained, which may be tested by weighting the same from about every other inch in length. By this means a very good indication will at once be formed whether any liquation has proceeded the casting, on account of the inconsistency either of the metal or alloy that has thus been treated. These paper moulds are not intended for metals above the melting-point of zinc; for copper, iron, &c., asbestos sheeting should be used in its stead.

Combustion-Tubing (how to preserve).

During a tube combustion, employing the ordinary glass tubing in general use for that purpose, direct contact of the contents will oftentimes be observed to cause, either whilst hot, or when cold, a fracture of the glass, and thus prevent further use of the same; a thin strip of asbestos placed next to the glass will, in many cases, prevent breakage, and thus preserve the same tube for

various further operations. Many combustion estimations may be accurately performed in an iron tube.

Unsuspected Impurity of Acids.

The impurity of the various commercial acids are generally well known, and the foreign substances most frequently found contaminating them are naturally sought for before employing the purer acids. As a rule, however, nitric acid, excepting small quantities of sulphates and chlorides, is usually supposed to escape contamination. I may, however, mention that I have frequently detected selenium in a so-called pure acid. As the acid was intended for parting gold, on account of the vigorous way in which selenic acid attacks that metal, it might, if it had escaped detection, cause considerable errors. It would be interesting to know to what extent of division the millionth part of a grain of gold would become if subjected to such an impurity.

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18, Albion Street, Everton, Liverpool.

THE COLOURATION DETERMINATION OF NITRIC ACID BY MEANS OF A SULPHURIC SOLUTION OF DIPHENYL-AMINE.

By J. A. MÜLLER.

THE blue colouration first observed by W. Hofmann, which diphenylamine gives with nitric acid, and which is produced with other oxidisers, has been used for the colorimetric determination of nitrous and nitric acids. E. Kopp was the first to utilise this reaction of nitrous acid for its estimation in the sulphuric acid of commerce. R. Böttger recommends the reaction of Kopp for detecting nitrites or nitrates in potable waters. H. Settegast uses Vierordt's spectrophotometer to observe the absorbing power due to the intensity of the blue tint produced on pouring 1 c.c. of the aqueous solution of a nitrate into 9 c.c. of sulphuric acid containing one-thousandth part of diphenylamine, and makes use of it to determine the quantity of nitric acid contained in a watery solution when this quantity varies between 1 and 40 millionths of NO_2H .

More recently L. Spiegel has sought to effect the same determination by direct comparison, using standard solutions of nitric acid (in the state of potassium nitrate?). On operating as Herr Spiegel indicates in his memoir the author finds that the sensitiveness of the reaction is not satisfactory for solutions containing 0.5 grm. to 2 m.grms. N_2O_5 per litre, and that the colour only reaches its maximum intensity after about ten hours.

The author has made a number of experiments to determine the conditions which must be observed to obtain the greatest sensitiveness in the reaction. In the first place all the oxidisers which give a blue colour with a sulphuric solution of diphenylamine, care must be taken that the liquid in question contains no oxidising agents save nitric acid. The blue colour is not interfered with by a small quantity of hydrochloric acid, but it is modified, or even destroyed, by hydrobromic or hydriodic acids. Hence the colorimetric determination is not possible in presence of these latter acids.

According to Spiegel, organic matters have no influence on the intensity of the colour produced. The author has found that the addition of some drops of a solution containing 7.5 per cent of dextrine (commercial) to a liquid coloured with 0.003 m.grm. of nitric anhydride, turns the original blue tint to a green; after twenty-four hours the liquid was decolourised. The intensity of the blue colour produced on pouring an aqueous solution of nitric acid or of a nitrate into a sulphuric solution of diphenylamine varies for a given quantity of the oxidising agent with the proportion of diphenylamine and the concentration of

the sulphuric acid employed. With a very dilute acid it is not produced at all. For very dilute solutions of nitric acid or of nitrates the author has obtained good results by pouring 1 c.c. of the aqueous nitric solution into 5 c.c. of concentrated sulphuric acid containing 0.001 gm. of diphenylamine.

The following is the method of effecting a colorimetric determination:—

Into a test-tube of 15 centimetres, perfectly clean, there are poured 5 c.c. of the sulphuric solution of diphenylamine at 0.2 gm. of diphenylamine per litre of pure strong sulphuric acid and 1 c.c. of the solution of the nitrate under examination. The tube is shaken and, after a moment, the blue tint is observed; it should be very light. If not, the solution of nitrate is diluted until a new trial gives this result. With a little experience we may thus easily obtain solutions containing from 0.5 to 5 m.grms. of nitric anhydride per litre, and even form an approximate judgment of the quantities between these two limits. To determine this quantity more exactly, a number of trials were made with standard solutions of potassium nitrate contained in ten bottles, 0.5, 1, 5 m.grms. N_2O_5 (in the state of nitrate) per litre. We then, after about an hour, compare the colourations obtained with the solution under examination and those given by pure solutions of potassium nitrate. The results are not comparable except we operate as accurately as possible under the same conditions.

With solutions containing from 0.5 to 2.5 m.grms. of nitric anhydride per litre we may thus appreciate differences of colouration due to 0.5 m.grm. N_2O_5 ; at 2.5 m.grms. or at 5 or 6 m.grms. we can no longer observe differences of colour due to difference below 1 m.grm. of nitric anhydride per litre; up to 10 to 12 m.grms. of nitric anhydride per litre the blue colourations are too deep to be useful.

If, along with the nitric acid to be determined, there is a notable quantity of nitrous acid, it is oxidised with permanganate and the total nitric acid is then determined colorimetrically.

This method of determination may serve for the estimation of small quantities of nitric acid in arable soils or in drainage water, but the solution operated upon must be perfectly clear.—*Bulletin de la Société Chimique de Paris.*

THE TREATISE OF DEMOCRITUS ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

(Continued from p. 89).

XI. O! NATURES, governors of natures! O! natures, how great, conquering natures with their changes! O! natures above Nature, delighting natures! Therefore these are great natures; no others are more excellent among tinctures than these natures; none are like, none are greater, all these take effect as solutions. You therefore, O! wise men, I plainly understand are not ignorant, but rather wonder, since ye know the power of nature. but the young men are much in error, and will not put faith in what is written, since they are ignorant of matter, not noticing that physicians where they wish to prepare a useful drug, do not set about making it inconsiderately, but first test it, whether it is warming, and how much cold, or humid, or other substance necessary, joined with it will make a medium temperament.* They, on the other hand, boldly and inconsiderately desiring to prepare that valuable medicine and ending of all diseases, do not learn that they are running into danger. As they consider that we speak in fables and not mystically, they display no diligence in inquiring into the species of

things. For example, if this is cleansing, but that unimportant; and if this is fitted to receive a colour, but that to prepare (for receiving it); and if this tinges the surface, or if the tincture gives off an odour from the surface, or vanishes from the interior of the metallic body; or if this resists fire, but that mixed with anything enables it to resist fire. For example, if salt cleanses the surface of *Jove** it cleanses its interior parts; and if the exterior part contracts rust after the cleansing, the interior parts do so also; and if mercury whitens and cleanses the surface of *Venus*,† it whitens also the interior; and if it leaves the exterior, it leaves the interior also. If the young men had been skilled in this kind of knowledge, applying their minds judiciously to the actions of substances, they would have suffered less loss; they know not the antipathies of nature, that one species may change ten, as a drop of oil stains much purple, and a little sulphur burns many things. Let these things be said, therefore, of medicines,‡ and of the extent to which what is written may be relied on.

XII. A GOLD VARNISH FOR SILVER.

Let us deal with liquids in their turn. Taking Pontic rhubarb, rub it up in bitter Aminean wine to the consistency of wax, and take a thin piece of *Luna* to make *Sol*, the pieces of which may be a full nail in breadth, that thou mayest use the drug again and again; place it in an empty vessel, which, luting on all sides, gently heat from beneath until the middle (of the leaf) is reached. Then place the leaf in the remainder of the drug, and complete the action with the aforesaid wine, as long as the liquid appears thick. In this, throw at once the uncooled leaf, and allow it to absorb, then take it and place it in a crucible, and thou shalt find *Sol*.

But if the rhubarb be dried with age, mix it with equal parts of celandine, preparing it, as of custom, for celandine has a relationship to rhubarb. Nature rejoices with nature.

XIII. ANOTHER GOLD VARNISH.

Take crocus of Cilicia,§ and leave it with the crocus flower, and the aforesaid juice of the vine, and thou shalt have a liquor, as is accustomed to be done. Colour silver, cut into leaves, until it seems shining to thee. But if the leaf be bronze it will be better, but first cleanse the bronze, as customary. Then taking two parts of the herb aristolochia, and double of crocus, and celandine, make it of the consistency of wax, and anointing the sheet, do as before, and wonder, since the crocus of Cilicia has the same effect as mercury, as also cassia with cinnamon. Nature conquers nature.

XIV. ANOTHER GOLD VARNISH.

Taking our lead made shining by Chian earth, and pyrites, and alum, burn with chaff, and melt into pyrites; and rub up crocus and cnicum, and the flower ocumenicus with the sharpest vinegar, and make a liquid, as of custom, and dip the lead into it, and allow it to absorb it, and thou shalt find *Sol*, but let the composition have a little unburnt sulphur; for nature conquers nature.

XV. This is the plan of Hepammenes, which he showed to the priests of Egypt, and it remains to the times of these philosophers, the matter of the Chrysopoeia. Nor should ye wonder if one thing performs a mystery of this kind. Do ye not see that many drugs can with difficulty, even in the progress of time, heal up wounds produced by iron, but human excrement succeeds in no long interval of time; and many drugs employed for burns produce often no good, and most in no way diminish the pain, but lime alone, when rightly prepared, drives out the ailment; and if various cures are tried for ophthalmia, they generally increase it, but the plant buckthorn, used to all sickness

* Greek, copper.

† Greek, orichalium.

‡ Greek, dry pow. substances.

§ Is this the bulb, for which Cilicia was famous, or a yellow metallic compound?

* Alluding to the four principles of nature: warm, cold, dry, and moist, by the combination of which the four elements were formed.

of this kind, cures perfectly. Vain and unsuitable matter should therefore be despised, but things be used according to their natures. Now therefore learn from these also, that no one has ever been successful without the aforesaid natures. But if nothing can be done without these, why do we desire a forest of many things; what is our need of the concourse of many species for the work, when one surpasses all?

Let us now see the composition of the species from which silver can be made.

(To be continued).

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,

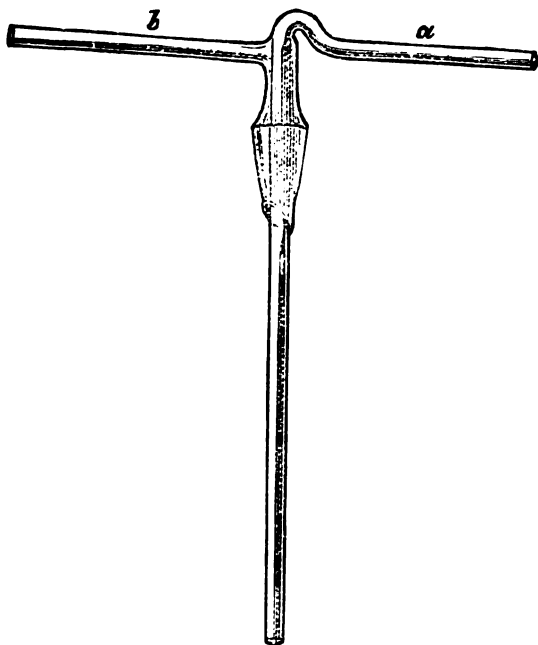
Professor of Chemistry in the University of Virginia.

(Continued from p. 82).

General Precautions Observed in the Experiments for the Determination of the Atomic Weight.

ALL the reagents used were prepared or purified by myself, and most carefully tested for any traces of such impurities as might reasonably be suspected, and as could

FIG. 1.



affect their application to the purpose in view. Particular care was bestowed upon the examination of the distilled water, acids, and other materials used in large quantity. To remove organic matter from the water required, it was distilled from a small amount of potassium permanganate and sulphuric acid.

Scrupulous care to exclude atmospheric dust was observed. In the evaporation of some of the gold solutions the process was carried out in a glass bottle of considerably larger capacity than the volume of liquid to be treated, furnished with a well ground glass stopper of special construction, as shown in Figs. 1 and 2, the latter representing the stopper in place. Air, purified by passing through a red-hot tube, then through a solution

of potassium permanganate and sulphuric acid, and dried by passing through concentrated sulphuric acid and over solid potash, was introduced by the tube *a*, which went down to near the level of the liquid to be evaporated, while this air, charged with vapour of water from the liquid, was withdrawn through the tube *b* by means of a water-jet pump; the bottle was moderately heated by immersion to the greater part of its height in a water-bath.

In filtering the gold solutions no paper or other organic material was used, but fine white siliceous sand, previously boiled in nitric and hydrochloric acids, washed with water, and well ignited to burn off any organic matter, was substituted, supporting it on coarser sand and larger fragments of quartz, similarly purified, and the whole arranged so as to prevent the possibility of any sand grains being mechanically carried into the filtered liquid. Vessels of hard glass and Berlin porcelain were employed. Care was taken to work in a clean laboratory atmosphere, from gases or vapours which might affect the materials dealt with.

First Series of Experiments.

A neutral solution of auric chloride was prepared by cautiously heating auric chloride, made, as suggested by Julius Thomsen, by the direct action of pure chlorine

FIG. 2.



upon finely divided metallic gold, until such an amount of chlorine had been given off that on treating the residual material with moderately warm water, metallic gold only remained undissolved, which was then filtered off. This neutral solution having been rendered uniform by agitation, two approximately equal portions of it were weighed off, using, of course, stoppered vessels to prevent evaporation during the weighing. From one of these portions the gold was thrown down in the metallic state by pure sulphurous acid with the aid of heat, carefully collected, well washed, dried, ignited in a Sprengel vacuum, and weighed. To the other portion there was added the carefully prepared solution in a minimum of nitric acid of an accurately weighed quantity of pure silver, a little more than equivalent to the chlorine present, the liquid

* A Paper read before the Royal Society, May 9, 1889.

and precipitate digested together for a considerable time with gentle warming in a stoppered glass flask, well agitated from time to time, and the precipitate (of silver chloride, containing also the gold) filtered off upon siliceous sand, and thoroughly washed, avoiding throughout the decomposing influence of light. The clear filtrate was nearly neutralised with pure sodium hydroxide (from metallic sodium), evaporated down to a small bulk, using the vessel represented in Fig. 2, and finally the remaining silver was determined (with all the needful precautions of the silver assay) by means of a weighed quantity of a weak solution of pure hydrobromic acid standardised against pure silver. This mode of determining chlorine by means of silver and hydrobromic acid was suggested to me in a letter, of the 27th January, 1887, with which I was favoured by M. Stas,* who advocates it as the most exact process available. The pure silver required was prepared in the same way as that used in my experiments on the atomic weight of aluminum,† and was heated in the Sprengel vacuum to remove all occluded gas. The hydrobromic acid was prepared as directed by Stas in his published paper—"De la Détermination du rapport proportionnel entre l'argent, les Chlorures et les Bromures."‡

In reporting the results obtained, the quantity of gold stated is that actually weighed, but the quantity of silver corresponding thereto has, for the sake of simplicity, been given as that required for an exactly equal quantity of the auric chloride solution, while, as stated above, the quantity of liquid weighed off was very nearly, but not exactly, equal to that from which the gold was thrown down, the difference being allowed for in calculation.

With this explanation the results of the first series of experiments were as follows:—

Experiment.	Character of gold used.	Gold. Grms.	Silver required to precipitate Cl. Grms.
I.	A, a	7.6075	12.4875
II.	A, b	8.4212	13.8280
III.	B	6.9407	11.3973
IV.	A, c	3.3682	5.5286
V.	C	2.8244	4.6371

In regard to conceivable sources of error connected with this method, it is to be observed that, in preparing the original auric chloride solution, if there should be any reaction between this gold salt and the water, leading to the formation of traces of hydrogen auri-chloride and precipitation of a little auric oxide or hydroxide, which might escape observation in admixture with the metallic gold left undissolved, the tendency would be to lower the atomic weight found for gold. If, by reaction between this residual metallic gold and the auric chloride solution, any traces of aurous chloride were produced and taken up by the solution of the higher chloride, the effect would be to raise the apparent value of the atomic weight.§

If, in the reaction of the silver solution upon that of auric chloride, partial withdrawal of chlorine should lead to the formation of any traces of aurous chloride, precipitated along with the chloride of silver, and not afterwards decomposed during the digestion of the precipitate with the remaining solution, the resulting error would also be in the direction of too high an atomic weight. The probability of the last supposition is diminished by an excess of silver for the whole amount of chlorine present having been added at once. It is not very likely that any one of

these defects actually belongs to the method and affects its results to a sensible extent. Of the three, I should be more inclined to suspect the possibility of the second than either of the two others.

Second Series of Experiments.

A neutral solution of auric bromide was prepared by a like process to that used in making the auric chloride of the first series; adding upon pure metallic gold with pure bromine (prepared with the precautions recommended by Stas), evaporating the solution to dryness, out of reach of dust, cautious heating of the residue, re-solution of auric bromide, and filtration from undissolved metallic gold.

Two nearly equal portions of the solution were accurately weighed off, and treated as described above; in one, reducing the gold to the metallic state and determining its weight; treating the other with a small excess of silver in solution as nitrate, filtering off the precipitate, concentrating the filtrate with the precautions already described, and determining in it the excess of silver by means of hydrobromic acid.

Reducing the amounts of silver actually used to the corresponding quantities for portions of auric bromide solution exactly equal to those from which in each case the gold was obtained, the results in six experiments stood as follows:—

Experiment.	Character of gold used.	Gold. Grms.	Silver required to precipitate Br. Grms.
I.	A, b	8.2345	13.5149
II.	A, c	7.6901	12.6251
III.	B	10.5233	17.2666
IV.	A, a	2.7498	4.5141
V.	C	3.5620	5.8471
VI.	A, b	3.9081	6.4129

In these experiments the sources of constant errors which suggest themselves as possible are essentially similar to those of the first series; but, if any such really exist, there is, of course the likelihood of some difference being introduced by the substitution of bromine for chlorine. Hence the desirability of multiplying experiments in this modified form.

Third Series of Experiments.

For these experiments potassium auri-bromide was prepared with great care from an excess of metallic gold treated with bromine and potassium bromide, purified in accordance with Stas's suggestions, and the double salt five times re-crystallised. The last crystallisation was conducted fractionally, in closed vessels, with special care to exclude dust, by gradual but pretty rapid cooling with agitation, and the earlier and later portions separated out were kept apart in after use.

For each atomic weight determination an unweighed quantity of this potassium auri-bromide was dissolved in water, the solution rendered uniform by agitation, and divided into two nearly equal parts, which were severally weighed with accuracy, and in one the gold reduced to metal as in the experiments of the first and second series, and in the other the total bromine precipitated by silver solution as before, the comparison being made once more between the weight of the gold and that of the silver equivalent to the bromine (in this case representing 4 atoms) existing in the double bromide.

Again stating the quantities of silver corresponding to portions of the auri-bromide solution exactly equal to those used in determining the gold, the following were the results obtained:—

Exp.	Character of gold used.	Fraction of crystallised auri-bromide used.	Gold. Grms.	Silver required to precipitate Br. Grms.
I.	A, b	First	5.7048	12.4851
II.	A, b	Second	7.9612	17.4193
III.	B	First	2.4455	5.3513
IV.	B	Second	4.1032	9.1153

* In this letter M. Stas says:—"Je me permets de vous recommander l'emploi de l'acide bromhydrique pour la précipitation de l'argent resté dans un liquide après une double décomposition opérée à l'aide d'un chlorure et d'un sel d'argent. On réussit à condition que l'eau mère renferme un excès d'argent dont le poids est le triple du métal qui peut rester en solution à l'état de chlorure d'argent."

† Phil. Trans., 1880, p. 1020.

‡ Mémoires de l'Acad. Royale des Sciences de Belgique, vol. xliii., 1882.

§ These two remarks apply, of course, also to Krüss's first series of experiments.

Of the tendencies to constant error which may be imagined in connection with the experiments of the first two series, and which have been noticed above, the first may probably be considered as not applying to the method pursued in this third series, while the second and third might still be applicable. But the superior stability of the double salt constitutes an advantage in its favour, and, as it formed the chief material for the experiments of Krüss and of Thorpe and Laurie, a comparison with their results is desirable, the mode of treatment pursued by me in ascertaining the composition of the salt not having been quite the same as that used by these chemists.

Fourth Series of Experiments.

A weighed quantity of trimethyl-ammonium aurichloride $[N(CH_3)_3HAuCl_4]$ was decomposed by heating in the air, and the weight of the residual metallic gold determined. This trimethylamine salt was selected because the base is of simple and well established constitution, and may with reasonable probability be counted upon as obtainable in a state closely approaching purity, and because the gold salt is easily crystallised, possesses a considerable degree of stability, and contains approximately half its weight of gold, so as to offer the most favourable chance of determining with accuracy the ratio between the metal left behind and the sum of the remaining constituents driven off on ignition. Although its use in fixing the atomic weight of gold involves the atomic weights of three other elements—carbon, nitrogen, and chlorine—all three of these constants deserve to be ranked amongst those already known with the nearest approach to precision at present attainable.

In order to obtain pure trimethyl-ammonium chloride, the impure commercial salt, derived from the *vinasse* of beet-root sugar-making, was used, first setting free and distilling off a considerable quantity of trimethylamine and condensing at about the right temperature, and subsequently purifying the product by Hofmann's method of treatment with ethyl oxalate and renewed distillation. The purified trimethylamine was several times fractionally distilled, and the portion of correct and most constant boiling-point finally neutralised with pure hydrochloric acid. The concentrated solution of trimethyl-ammonium chloride was now precipitated by a strong solution of auric chloride, the mother-liquor decanted off, and the gold re-dissolved in hot water, and re-crystallised several times. The bright yellow crystalline powder was dried, first over sulphuric acid, and afterwards over phosphorus pentoxide, until it ceased to lose weight; towards the end of the drying the temperature of the vessel was raised to about $50^\circ C$. Preliminary experiments seemed to indicate the probable existence of this salt crystallised with a single molecule of water, but most of that prepared contained no constituent water, and it appeared easy to attain complete drying without any decomposition of the salt itself. Throughout its treatment the salt, which was not in any high degree hygroscopic, was well guarded from dust and from any possible decomposing effect of light.

The portion of the salt to be used in each experiment was contained in a small glass-stoppered weighing flask, which was removed just before it was needed from the phosphorus pentoxide desiccator, the stopper having been inserted; the flask was weighed, the greater part of its contents transferred quickly to a weighed porcelain crucible, the stopper at once replaced, and, the flask being again weighed, the quantity of gold salt taken from it was found by difference.

In order to avoid mechanical loss by spluttering on igniting the crucible and its contents, the aurichloride lying together at the bottom of the crucible was covered by a layer, nearly a centimetre deep, of clean, carefully purified, and just previously well-ignited siliceous sand, the weight of this sand being known by taking it from a weighing flask in which it had been cooled over phosphorus pentoxide, and noting the loss of weight of this flask. In applying heat to the crucible and its contents it was found necessary to heat gently for a long time, raising the temperature slowly, in order to prevent extensive charring at the bottom. Then, before the temperature had become too high, but after a considerable part of the volatile matter had been driven off, the sand was carefully stirred in with the remaining material so as to produce pretty uniform mixture, in order that the gold might not undergo partial welding together at a higher temperature, which might have led to wrapping up particles of carbon and their protection from combustion. In this operation a very small porcelain stirrer was used, as a platinum wire would have welded on and taken up some of the metallic gold; the weight of this stirrer was determined in advance, and checked after use. Finally, the contents of the crucible were submitted to very careful and prolonged heating to moderate redness, with free access of air and occasional cautious stirring, so as to burn away every trace of carbon. After cooling in a desiccator, the crucible and its remaining contents were weighed, giving the weight of the residual gold by subtraction of the weights of the crucible itself and the siliceous sand. As an additional safeguard against any particles of carbon left unburned escaping detection, the gold was afterwards dissolved out with aqua regia, and the white sand carefully looked over with a lens.

The results of five experiments thus conducted were as in Table below.

In these experiments the most probable source of error may be fairly taken as arising from the presence of traces of methyl-ammonium or dimethyl-ammonium aurichloride with the trimethyl-ammonium salt. I know of no direct evidence that any such impurity was present, and the absence of any such evidence in the results from the earlier as compared with the later crops of crystals rather tells against the supposition of its presence, but one cannot feel certain of its entire absence. If present, its effect would be to raise the atomic weight obtained for gold. It is also conceivable that there may have occurred volatilisation of gold to a minute extent as auric chloride, in accordance with the observation of Krüss that this salt may be sublimed in small quantity at moderate temperatures in a stream of chlorine; but, there being no such stream of chlorine in these experiments, and, on the contrary, the decomposing action of the hydrogen of the trimethylamine salt, this does not seem likely; the effect would, of course, be to raise the atomic weight obtained for gold. Another possible cause of error might consist in imperfect drying of the gold salt used, but the constancy of weight attained on drying renders it unlikely that any other than extremely minute error should come of this, though not altogether excluding the possibility of its occurrence; its tendency would, of course, be to lower the atomic weight obtained. Any trouble from hygroscopic moisture on the surface of the porcelain crucible and sand was, I think, satisfactorily guarded against by the use of a corresponding tare crucible, and by more than one weighing after a near approach to the true figures had been obtained, the crucibles having meanwhile been restored to the desiccator

Experiment.	Character of gold used.	Character of gold salt used.	Salt ignited. Grms.	Residual gold. Grms.	Loss by ignition. Grms.
I.	A, b	Earlier crop of crystals	14.9072	-7.3754	=7.5318
II.	A, b	Middle " "	15.5263	-7.6831	=7.8432
III.	A, b	Last " "	10.4523	-5.1712	=5.2811
IV.	C	Middle " "	6.5912	-3.2603	=3.3309
V.	C	Last " "	5.5744	-2.7579	=2.8165

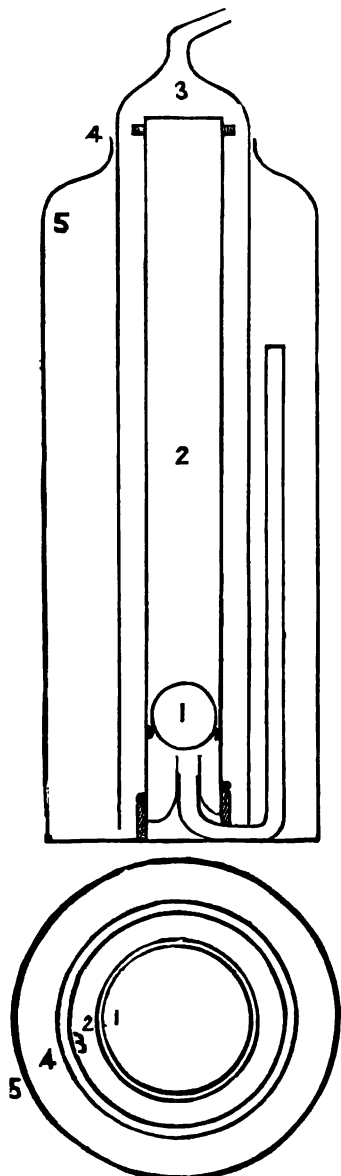
and kept therein for some time. The precautions taken seemed to afford sufficient protection against any merely mechanical loss during the ignition.

(To be continued).

SULPHURETTED HYDROGEN GENERATOR.

By W. OAKES KIBBLE.

I HEREWITH enclose a sketch of my improved H_2S generator. The advantages claimed are as follows:—1. Simplicity—hence cost small. 2. Sulphide is effectively prevented from entering main body of acid, thus saving



1, Glass Ball.

waste and smell. 3. Very easily re-charged and cleaned. 4. Store of gas is always ready. 5. When not in use automatically the action ceases. 6. A continuous supply

at a moderate pressure—4 inches in water in smallest to 8 or 12 inches in larger. 7. If any part broken, can be renewed at a proportional cost. 8. The acid being used from the top, the specifically heavier spent acid does not interfere with working of apparatus even after standing for days. 9. No direct escape of gas. 10. Compactness.

Parts and Functions of Apparatus.—Inner tube with studs holding glass ball (loosely fitting); this supports sulphide of iron. The bottom is closed and a tube sealed in, thus forming an effectual trap for the small particles of sulphide. An outer tube drawn out for attachment of rubber tube and tap or pinch-cock. A glass tube (thin) from the trap into which it fits, reaching three-fourths of the way upon the outside. A rubber collar at the bottom and band at the top of inner tube to prevent jarring. An ordinary broad necked reagent bottle to hold acid. A rubber ring is fitted three-fourths of the way round in the neck to prevent outer cylinder from rising.

To use, fill jar three-fourths full of acid (dilute), then put in inner tube filled with sulphide, and slip outer tube over it; shut tap or close pinch-cock. The acid which has entered immediately acts on the sulphide, generating H_2S , which fills the tubes, leaving the sulphide practically dry, any pieces of sulphide falling past 1 being dissolved. As the gas is used acid re-enters and generates fresh supply.

It will shortly be obtainable in sizes from 10 in. high 3 in. diameter to 20 in. high and 7—8 in. diameter, the capacity of the smallest being about 1 litre and the largest about 10 litres.

Finsbury Technical College,
Leonard Street, City Road.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, February 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 189 samples examined were found to be clear, bright, and well filtered.

During the first month of the new year the quality of the water supplied to the Metropolis has not shown any retrogression, but has continued to be of the same high character (exceptionally high for the period of the year) as recorded in our previous monthly report. Taking the estimations of organic matter present, of oxygen required for its oxidation, and of degree of colour tint, while one

item has shown a slight increase, and another a slight decrease, the variation in each case is within very narrow limits. As regards the water furnished by the Companies taking their supply from the Thames, the maximum amount of organic carbon found in any single sample examined was 0.146 part in 100,000 parts of the water, as against a maximum of 0.153 part, and a mean of 0.143 part in the previous month's entire supply.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 21st, 1890.

Prof. G. CAREY FOSTER, F.R.S., Past President,
in the Chair.

Mr. S. EVERSHED was elected a member of the Society.

The following communications were read:—

"On a Carbon Deposit in a Blake Telephone Transmitter." By F. B. HAWES.

The author exhibited photographs of the interior portions of the transmitter on which the deposit had taken place. These portions consist of a metal diaphragm, a highly polished carbon button, and a platinum contact piece carried by a German silver spring placed between them. The diaphragm presented a mottled appearance, due to the deposit, but the part which had been behind the German silver spring seemed comparatively clean. The deposits on the carbon button and German silver spring were much less dense than that on the exposed parts of the diaphragm, and the space near the point of contact between the platinum and carbon was free from deposit. The deposit was fairly adherent, considerable rubbing being necessary to remove it, and, on examination under the microscope, particles of copper and metallic crystals could be seen. The author believes the deposit due to some kind of bombardment of carbon particles, but was unable to say why it should occur, or why the varnished diaphragm should receive the greater deposit, although it was further from the carbon than the German silver spring.

Mr. C. V. BOYS said the photographs reminded him of a phenomenon he observed some time ago on a glass sheet against which one terminal of a dry pile had been resting for some weeks. Just as on the carbon button, the glass near the point of contact was clean, and has a comet-shaped deposit formed around it. He could offer no explanation of the appearance.

"The Geometrical Construction of Direct Reading Scales for Reflecting Galvanometers." By Mr. A. P. TROTTER.

In a recent paper "On Galvanometers," by Prof. W. E. AYRTON, F.R.S., T. MATHER, and Dr. W. E. SUMPNER, read before the Society, the opinion was expressed that proportionality of scale reading to current was very desirable, and the present paper shows how to bend a scale of equal divisions so as to give the required proportionality. Suppose the currents required to produce several deflections have been experimentally determined. A full size plan of the scale is then drawn, and radial lines from the points on the scale at which the observations were taken are drawn towards the centre of the mirror. Let these radii be numbered 0, 1, 2, 3, &c., commencing from zero-azimuth. According to the procedure recommended, distances proportional to the

several current strengths are marked off along the edge of a strip of paper, a few inches being left over at each end. Call the marks *a, b, c, d, &c.*, *a* being the zero point. Two points on the radii 0, 1, and equidistant from the mirror, are now found such that the distance between them is equal to that between *a* and *b* on the strip, and the points marked by fine needles stuck in the board. The zero end of the strip is now fixed, so that the marks *a* and *b* lie against the needles, and the strip is swept round until the mark *c* coincides with the radius 2, where also a needle is placed. Repeating the process gives a series of points which, on being joined, form part of a polygon. A line can then be drawn between the inscribed and circumscribing curves, which has the same length as the sum of the straight lines; and this is the curve to which the original scale may be bent, so as to give proportional readings. Diagrams showing such curves constructed from the calibrations of instruments given in the paper above referred to, accompany the paper.

The author showed that a family of curves may be drawn, each of which satisfies the required condition. Of the two limiting curves, one is tangential to the usual scale line at zero azimuth, and the other passes through the vertical axis of the mirror. The flattest of the various curves is generally the most convenient.

Mr. J. SWINBURNE asked whether good definitions could be obtained when such curved scale not equidistant from the mirror were used, and also whether it was not easier to divide a flat scale unequally, so that the readings are proportional to the current.

Mr. TROTTER, in reply, said Dr. Sumpner thought there would be no difficulty as regards definition with the flat curves shown. He (Mr. Trotter) also added that a curved scale might be advantageous in reading the deflections from one side of a table, as the more distant part of the scale could be more nearly perpendicular to the line of sight. For such an arrangement, however, a parallel beam of light would be required.

"A Parallel Motion suitable for Recording Instruments." By Mr. A. P. TROTTER.

This is a modification of Watts's parallel motion, in which the two fixed centres are on the same side of the line described by the "parallel point." The arrangement consists of two vibrating arms, one of which is twice the length of the other, and whose outer ends are jointed respectively to the middle and end of a short lever; the free end of the latter describes an approximate straight line. The motion was arrived at by considering the curve traced out by a point on the radius of a circle, such that its distance from the circumference, measured towards the centre, is equal to the radial intercept between the circle and a tangent line. The equation to the curve is $r = 2 - \sec \theta$ (conchoid of Nicomedes), and the radius of the osculating circle at the point where the intercept is zero is given as half that of the initial circle. This osculating circle, the author finds, practically coincides with the curve over a considerable angle (40°), and therefore may replace this part of the curve; hence the motion.

The author thinks the motion will be useful for recording barometers, ammeters, and voltmeters, as it is more compact than that of Watt, and needs no fixed point beyond the straight path.

Owing to the absence of Prof. S. P. THOMPSON his paper "On Bertrand's Refractometer" was not read.

Detection of Free Chlorine in Hydrochloric Acid.—G. A. LE ROY.—The author recommends the use of metallic copper or phosphorus, and also diphenylamine or phenylamine. The acid containing infinitely small traces of chlorine, if treated in a test-tube with a few particles of chlorine, takes immediately a blue colour.—*Bull. de la Soc. Chim. de Paris*, Vol. II., No. 11.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By T. E. THORPE, B.Sc. (Vict.), Ph.D., F.R.S., Treas.C.S., Professor of Chemistry in the Normal School of Science and Royal School of Mines, South Kensington. Assisted by eminent Contributors. In Three Volumes. Vol. I. London: Longmans, Green, and Co.

THIS work, as we learn from the preface, is intended to be complementary to the new edition of "Watts's Dictionary of Chemistry." Many of the articles inserted—we may, perhaps, most prominently signalise those on the coal-tar colours and their raw materials—are of remarkable excellence. Others, again, not less ably written, may be regarded as of questionable relevance. We should certainly be slow to undervalue a study of the "rare earths." But until they can be procured in much greater quantity than at present, a consideration of the "Cerium Metals and Earths" can have little interest for the technical chemist.

The elaborate article on the balance is also of doubtful relevance. Indispensable as this appliance is to every chemist, its construction does not depend on chemical principles, and hence the carefully written and freely illustrated description here to be found seems out of place.

Of remarkable value are the sections on indicators, in connection with alkalimetry and acidimetry, and accompanied by a tabular view of the conditions under which each gives trustworthy results. It will scarcely be believed that no longer than thirty-five years ago the indicator used by a commercial analyst whose valuations of soda-ash were greatly admired by brokers, was his tongue!

The article on albumen does not omit the important caution that, in the manufacture of blood-albumen, all agitation must be avoided. If the climate were colder the best place in the world for the manufacture of blood-albumen would be Fray Bentos, where the blood might be conveyed directly from the slaughter-houses to the works.

Under "Alcoholometry" we find no condemnation of the "proof spirit" still absurdly used in Britain as a standard both for fiscal and commercial purposes.

Alizarin forms the subject of an excellent chapter, in which are given representations of the absorption and spectra of alizarin and purpurin. This is an example which ought to be followed.

Aluminium and its numerous compounds are very fully and ably described. By an oversight the manufacture of alum from the aluminous shales of Whitby is represented as being still carried on.

The remark is made that if all the ammonia possible were recovered and collected from the beet-sugar works in Germany, it would amount to 15,000 tons of sulphate yearly. But this manufacture cannot be very lucrative in the long run, as the beet-root fields have to be supplied with combined nitrogen either in the form of ammonium sulphate or sodium nitrate. The case of using wool as source of potash is very similar.

The chapter on the azines and their derivative colours, on the azo-colours, benzene and its homologues, bromine, cellulose, cements, chlorine, and the cyanides, as also that on bleaching, are fully on a level with the present state of knowledge, and will be found trustworthy. Dyeing scarcely receives full justice; calico-printing is omitted, but it will probably be noticed subsequently under "Tissue-printing."

There is a copious table of the reactions of the most important colours when fixed upon the fibre.

Lovibond's tintometer is described and figured, as well as other appliances and processes for colorimetric investigations.

It is scarcely necessary to say that Dr. Thorpe's work

will be universally appreciated by technical and manufacturing chemists.

*On the Present Position of the Question on the Sources of the Nitrogen of Vegetation; with some New Results, and Preliminary Notice of New Lines of Investigation.** By Sir J. B. LAWES, Bart., LL.D., F.R.S., and Professor J. H. GILBERT, LL.D., F.R.S. London: Published for the Royal Society by Trübner and Co.

THE question of the supply of nitrogen to vegetation is one of the utmost importance, not merely from a theoretical but from a practical point of view. Put in a slightly different form it means, Are we, as far as the nitrogenous constituents of our frames are concerned, living on the earth's income, or, as in the case of coal, on its capital? Do plants depend for their growth on the combined nitrogen present in the soil and the sub-soil, supplied by manures and by the decomposing remnants of defunct organisms, or brought down by the rain in the form of ammonia or of nitric acid? Or are they able to fix in their tissues, directly or indirectly, any portion of the unlimited store of free nitrogen existing in the atmosphere? Such fixation might conceivably take place in various manners; by the direct action of the plant, by the mediation of fungi or microbia, by some reaction of constituents of the soil, by the silent electrical discharge, &c.

The subject has latterly received much careful experimental study at the hands of M. Berthelot, Dehérain, Joule, Dr. B. E. Dietzell, Prof. B. Frank, Prof. Hellriegel and Dr. Wilfarth, Prof. Emil von Wolff, Prof. W. O. Attwater and M. Boussingault, and of the authors themselves. The results cannot be pronounced decisive. Few authorities now, indeed, admit the direct condensation of free nitrogen. But certain observations, if they do not formally prove an indirect fixation do not so far give any decisive evidence to the contrary.

M. Berthelot thinks it proved by his experiments that vegetable soils, at least under the influence of the silent discharge, fix free nitrogen. The combination of nitrogen in the atmosphere itself is of course admitted, but its available limit in Europe has been approximately ascertained.

M. Dehérain has sought, during a period of ten years, to determine the loss or gain in the field under the influence of different manures, different crops, and different modes of cultivation. He records, in some cases, a loss of nitrogen, and in others a gain, but our authors, whilst fully admitting the accuracy of his analyses, entertain doubts concerning his method of sampling.

M. Joulie concludes that the fixation of free nitrogen is due to the action of microbia. Sir J. B. Lawes and Dr. Gilbert hold that such gains as M. Joulie finds within a lapse of fourteen months do not take place in ordinary agricultural practice.

Dr. Dietzell, in his cultivation experiments, finds, in every case but one with pears, and in every case with clover, a loss, not a gain, of nitrogen. Dr. Frank, like Dietzell, operated with soils exceptionally rich in nitrogen.

Prof. Hellriegel and Dr. Wilfarth conclude that the *Papilionaceæ* are less dependent than the *Graminæ* upon the soil as the source of their nitrogenous food. They accept Berthelot's view that the nodules on the roots of the *Papilionaceæ* swarm with microbia, which have the power of bringing free nitrogen into organic combination. Further confirmation, however, is necessary. In sterilised soils papilionaceous plants were as little capable of flourishing (in the absence of mineral manures) as vegetables belonging to other families.

Prof. E. von Wolff also finds a gain of nitrogen in experiments with the *Papilionaceæ*, but he admits that the amounts of absorption found in his experiments cannot be expected in agricultural practice, where the soil is

* Philosophical Transactions of the Royal Society of London, vol. clxxx. (1889) B, pp. 1-107.

not kept so porous. He ascribes the gain of nitrogen to the absorption of combined nitrogen from the air by the soils, as well as to the fixation of free nitrogen within the soil owing to the effects of porous and alkaline matter, rather than to the influence of microbia. He does not, at the same time, see his way to explain why other plants should not benefit by such absorption and fixation as well as the *Papilionacea*.

Prof. W. O. Attwater concludes that plants themselves are the agents in the fixation of nitrogen, as in his experiments the agency of electricity and of micro-organisms did not exist.

M. Boussingault has latterly re-examined the question, as in his former experiments the action of electricity and of micro-organisms was excluded. He writes to the authors that "If there is in physiology a fact perfectly demonstrated, it is the non-assimilability of free nitrogen of plants, even those of an inferior order, such as mycodermis and fungi."

In summarising the evidence on the question, the authors consider it decided that, since experimentation in the open air, instead of in closed vessels, has become more general, the evidence which is supposed to show the fixation of free nitrogen has become more plentiful. But the methods of explaining the facts are so conflicting that it is right to suspend judgment.

Underlying many of the experiments recently made is the assumption that there must exist some source of compensation for the nitrogen lost by the soil in the removal of crops. These losses seem to have been exaggerated. For Great Britain the average loss of nitrogen is probably under 20 lbs. per acre. A loss of nitrogen from the plants themselves is not proven, and the authors do not believe that it takes place. Sir J. B. Lawes and Dr. Gilbert think that the fungi are nourished chiefly by organic nitrogen, and that on their decay it becomes available for higher vegetation. Whether or not the microbia affect the combination of free nitrogen within the soil, they seem, at any rate, to bring the inert nitrogenous matter in the soil and subsoil into a condition assimilable by crops.

CORRESPONDENCE.

THE IGNITING-POINT OF SULPHUR.

To the Editor of the Chemical News.

SIR,—I must first express my sense of obligation to Professor Hodgkinson for his authoritative correction of the current mis-statements of the igniting-point of sulphur. Before writing my former note I had experimented on the subject, but being unable to quote the temperature observed, owing to its being above the range of the mercurial thermometer, I made no mention of my results. A brief account of the simple method used may be of some slight interest. The determination of the igniting-point of sulphur seems at first blush absurdly easy, and one naturally begins (particularly if one be impressed with a belief in its taking place at a comparatively low temperature) by heating some of the element in a small capsule standing on a hot plate and containing the bulb of a thermometer. One then notices that the sulphur volatilises freely much below its boiling-point, and, on continuing to heat, finds that it takes fire about 270° C. Careful observation at the moment of ignition clearly shows that the flame does not start at the surface of the fused sulphur, but proceeds from its vapour, which has flowed out of the capsule on to the hot plate, the temperature of which is, of course, considerably higher than that of the sulphur itself. It is to a failure to perceive this fact, that the statement usually adopted is due, some early experimenters having doubtless fallen into the error, and industrious copyists having perpetuated it.

Recognising the necessity of preventing the sulphur vapour from coming into contact with any object at a higher temperature than the sulphur from which it was derived, I placed my capsule in the centre of a hot plate one foot square, and surrounded it by a second plate parallel to the first, on which it was supported by little bits of tile, and having a central hole to accommodate the capsule, the fitting of the two being made good by judicious packing with slag wool. On heating the lower plate the temperature of the sulphur rose above the boiling-point of mercury without it showing the slightest tendency to catch fire, and ultimately it boiled before doing so. The large volume of vapour then arising sufficed to evade the barriers between it and the burner below, and transmitted the flame to the sulphur; but it was proved beyond question that, so far from sulphur igniting at a low temperature, it refuses to do so at all as long as it remains liquid, and the only fact that needs ascertainment is the temperature of ignition of gaseous sulphur.—I am, &c.,

BERTRAM BLOUNT.

Laboratory, Broadway,
Westminster, S.W.
Feb. 22, 1890.

ULTRA CREPIDAM?

To the Editor of the Chemical News.

SIR,—From a merely scientific point of view it would greatly interest me, and doubtless not a few of your readers, to see what comments your correspondents may have to offer on the following analysis of a water—which analysis was last week received and acted upon by the Local Board of a small country town:—

"I hereby certify that I have analysed the water from a well at . . . The following is a detailed result:—Physical examination: Clear, colourless, pleasant taste, and no smell. Microscopic: Nil. Chemical: Total solids, 7.9 grains per gallon; chlorine, 6 grains per gallon; ammonia free, 0.03 parts per million; ammonia albumenoid, 0.08 parts per million. Considering the amount of chlorine I must condemn this water as absolutely unfit for use; it presents clear and unmistakable signs of constant sewage pollution.—(Signed) ———, M.B.

P.S.—I may state that, except under exceptional circumstances, 1.5 grains per gallon of chlorine would render a water unfit for use."

I enclose my card and am, &c.,

R. R.

Feb. 21, 1890.

DETERMINATION OF OXIDE OF IRON AND ALUMINA IN PHOSPHATES.

To the Editor of the Chemical News.

SIR,—May we, through your columns, draw the attention of those of your readers interested in this question to a method for the determination of oxide of iron and alumina in phosphates, published in the *Zeitschrift f. Angew. Chem.*, 1889, 636—638, a reprint of which we received last November through the courtesy of the author—Mr. E. Glaser.

Mr. Glaser in his method avoids the use of acetate of ammonia or acetic acid, and therefore, on the one hand, any error from the solubility of phosphate of iron and alumina in free acetic acid, even when highly dilute; and, on the other hand, the difficulty of obtaining the phosphate of iron and alumina free from phosphate of lime. His process is to precipitate lime and magnesia as sulphates by addition of first excess of sulphuric acid and afterwards alcohol to render the removal of these bases as sulphates complete.

The alcoholic solution, after separation of the insoluble

sulphates by filtration, will then contain the whole of the oxide of iron and alumina, and also the phosphoric acid, with the excess of sulphuric acid, and the muriatic acid employed in dissolving the phosphate in the first instance. The alcohol is evaporated, and on the addition of a solution of ammonia in excess (the excess to be afterwards removed by boiling), the oxide of iron and alumina are precipitated and subsequently weighed as phosphates. The phosphoric acid in the weighed precipitate is determined, and the remainder will be the oxide of iron and alumina sought for.

For details of this "alcohol process" we refer your readers to Mr. Glaser's paper.

The correct determination of oxide of iron and alumina in the phosphates met with in commerce is, at the present time, a question of considerable importance to importers of mineral sulphate and manufacturers of superphosphate, and it is at the request of one of these that we trespass on your kindness in asking you to insert this letter,—We are, &c.,

E. F. TESCHEMACHER and J. DENHAM SMITH.

Highbury, London,
Feb. 21, 1890.

LARD.

To the Editor of the Chemical News.

SIR,—Just a few more words upon this subject. I quite expected a defender of the above would put in an appearance. If your correspondent, Mr. Brown, will look at my first letter, he will see that I say "Its common adulterant is cotton-seed oil, but we may look for many other foreign bodies and find them." I was not referring to stearin. I had in my mind such matters as starch, lime, suet, and others than cotton-seed oil, say, sesame, &c., oils. I say these substances have been, and still are, found in lard. It is all very well to talk of what the public expect; it is rather what they get. I am quite aware that the law says the public shall have wholesome articles of food, but the getting of them is another thing. Of course, when pretty well the whole of the hog is rendered down you may look for a "sloppy" article, termed lard; consequently "other matter" is mixed with it in order to get something like solidity. I object to this being called refined lard, or refined leaf lard—it is more like doctored dripping. What I term lard is that made from the flare or fat about the kidneys of the hog. It is no use to say dare not do so-and-so, that is all rhodomontade; such sophistication is done; and I again say something is wrong. I am quite content, after nearly thirty years' knowledge of the way articles of food have been, and still are, manipulated and adulterated, to know this. I shall be told next that there is no butter (not margarine) in the market which does not contain from 15 to 25 per cent of water; I say it is to be found. I have had my say, and will take leave of the subject.—I am, &c.,

JOHN H. SWINDELLS, Ph.D., D.Sc.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., No. 11.

New Researches on the Constitution of the Nitro-camphor- β and of the Chloronitrocamphor- α .—P. Cazeneuve.

On New Bases derived from Camphor: the Camphamine.—P. Cazeneuve.—The author heats 5 grms. of

normal monochlorocamphor- α with 20 grms. of saturated aqueous ammonia for twenty-four hours to 180° in a sealed tube. He obtains a blackish residue. From the solution of this matter after purification he obtains a body which crystallises in small needles radiating out from a centre. It melts at 180°, and is insoluble in water, but soluble in alcohol, ether, chloroform, and ligroine. This body is evidently of a basic nature, and its saline solutions give precipitates with all the general precipitants for alkaloids.

Monochlorocamphor obtained by Hypochlorous Acid; a New Monobromocamphor obtained by Hypobromous Acid; Constitution of the Monosubstituted Derivatives of Camphor.—P. Cazeneuve.—These papers have been, in substance, noticed already.

Influence of Certain Groups on the Valence of Oxhydryl and Carboxyl in the Aromatic Series.—P. Alexeyeff and E. Werner.—A thermo-chemical paper, not suitable for abstraction.

A New Hydrated Potassium Bisulphate.—J. B. Senderens.—The author ascribes to this compound the formula $S_2O_6.HO.KO + 11H_2O$. It melts at 30° and loses all its water of crystallisation at 100°, and is partially dehydrated even at a lower temperature.

Solubility of Saline Mixtures.—A. Etard.—The author explains his views by means of a diagram.

Chemical Studies published at the Session of the Hungarian Society of the Natural Sciences on October 12, 1889.—L. Illosvay de N. Illosva.—There is no ozone in oxygen prepared with strong sulphuric acid and potassium permanganate. The author further examines the formation of nitrous acid in certain special cases of active combustion, and the formation of cyanogen in the inverse case. He next examines the union of nitrogen and oxygen by means of platinum. Nitrogen combines with oxygen, even on the slow oxidation of iron reduced by hydrogen.

Action of Heat upon Chloralammonia.—A. Béhal and M. Choay.—On heating chloralammonia it is decomposed into chloroform and formiamide.

An Acid Cerium Sulphate.—G. Wyruboff.—The question of the atomicity and the atomic weight of cerium and the metals of its group is far from being solved. M. Mendeleeff proposes to change the formulæ of the two cerium oxides from CeO and Ce_2O_3 to Ce_2O_3 and CeO_2 . The atomic weight which, according to the recent researches of Buhig is 94.4, becomes thus 141.6. This view is confirmed by the determination of the specific heat, which Hillebrand found = 0.4479 between 0° and 100°, giving an atomic weight of 4.22 with $Ce = 94.4$, or of 6.34 with $Ce = 141.6$. The author holds that both physical and chemical properties contradict the hypothesis of Mendeleeff and support the older view.

Zeitschrift für Physikalische Chemie.
Vol. iii., Part 4.

Magnitudes of the Affinities of Organic Acids and their Relations to their Composition and Constitution.—W. Ostwald.—A continuation.

Determination of the Specific Gravity of Salts Soluble in Water.—J. W. Retgers.—The discrepancies in the published specific gravities of such salts are traced to the want of homogeneity of the salts in question and the imperfection of the method employed. To obtain perfectly homogeneous crystals of a salt, the author puts them in methylene iodide and dilutes the liquid gradually with benzene, stirring diligently. The crystals which sink first are selected. Being the heaviest, they may be considered the purest, being free from inclosed particles of mother-liquor and air. The sp. gr. of these selected crystals are then determined in Thoulet's liquid—a solution of potassium-mercury iodide in water.

Diffusion in Agar Jelly.—Felix Voigtländer.—Diffusion in agar galler from watery solutions is not disturbed by the process of imbibition. The validity of Fick's law for dilute solutions might be demonstrated at some length. The rate of diffusion of a substance in different concentrations of the agar jelly is alike. The constants of diffusion observed in the jelly are equal to those found for water, a larger and smaller. With a rise of temperature the constant does not augment, but the quantity of salt introduced increases in a linear proportion.

Reversible Transformation of Cupri-bipotassium Chloride.—W. Meyerhoffer.—This paper requires the accompanying plate and two woodcuts.

Relation of Pyrrol and its Derivatives to the Law of Raoult.—Gaetano Magnanini.—This memoir cannot be reproduced with the two accompanying illustrations.

Cryoscopic Behaviour of Solutions of Iodoform in Benzene and Glacial Acetic Acid.—Nik. von Klobulow.—The non-existence of the anomaly of iodoform mentioned by Raoult may be demonstrated with certainty.

Drop-Electrodes.—W. Ostwald.—A critique on the "Studies on the Chemical Theory of the Galvanic Element," published by F. Exner and J. Tuma in the *Berichte* of the Vienna Academy.

MEETINGS FOR THE WEEK.

- MONDAY, 3rd.**—Medical, 8.30.
— Society of Arts, 8. "Stereotyping," by Thomas Bolas, F.C.S.
— Royal Institution, 5. General Monthly Meeting.
TUESDAY, 4th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
WEDNESDAY, 5th.—Society of Arts, 8. "Recent Progress in British Watch- and Clock-making," by Julian Tripplin.
— Geological, 8.
THURSDAY, 6th.—Royal, 4.30.
— Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
— Royal Society Club, 6.30.
FRIDAY, 7th.—Royal Institution, 9. "Electrical Relations of the Brain and Spinal Cord," by Francis Gotch, Hon. M.A., Oxon., B.A., B.Sc.
— Geologists' Association, 8.
— Physical, 7. "On Bertrand's Refractometer," by Prof. S. P. Thompson.
SATURDAY, 8th.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
— Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

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The Directors of the Reading Gas Company are prepared to receive Tenders for the purchase of their TAR for One Year from the 1st of April next.

Specifications for the contracts can be seen at my Office, or will be sent on application.

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February 25, 1890.

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Prices to be given for Liquor from 8 to 16 ounces per 1000 gallons. Strength to be ascertained by the Distillation Process of Mr. F. W. Hartley, A.I.C.E.

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Payments to be made in cash, fortnightly.

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C. CROWTHER SMITH, Secretary.

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February 12, 1890.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1580.

M. LECOQ DE BOISBAUDRAN ON THE RARE EARTHS.

M. DE BOISBAUDRAN has contributed to the *Bulletin de la Société Chimique de Paris* a comment on my Presidential Address delivered before the Chemical Society in March, 1889. I must confess myself no little disappointed with my distinguished friend's reply. Considering the length of time at his disposal I had hoped, in the interests of truth, that M. de Boisbaudran would have been able to advance some novel and decisive facts—"instantia crucis," as Bacon called them—in support of his views. Such, however, does not appear to be the case. The memoir contains very little beyond a re-assertion of the statements which I considered in my Address.

I must point out as incorrect the following assertion:—"As this *savant* (i.e., myself) publishes sometimes in scientific journals which everybody is not obliged to read." The number of journals in which I publish my results is small: the *Transactions and Proceedings of the Royal Society*, the *Journal of the Chemical Society*, and the *CHEMICAL NEWS*. To these alone anyone who wishes to ascertain what are my opinions may refer.

The fluorescence method M. de Boisbaudran admits to be very delicate for the detection of slight traces, but he considers, curiously enough, that it becomes less sensitive when applied to "larger quantities of the same active matters." Too high sensitiveness is not often urged as an objection against any reagent, especially when the question is the recognition of substances which may occur only in infinitesimal traces.

The answer to the question why I did not try to eliminate manganese from my calcium sulphate prepared from Iceland spar is not hard to find: there was none to eliminate.

My learned friend does not appear to have thrown any new light on the yttrium question, nor does he succeed, to my thinking, in justifying his use of the term "yttria."

I will not, however, abandon the hope that M. de Boisbaudran and myself, in continuing our labours, may ultimately arrive at an agreement, based on truth, more complete than either of us has hitherto attained.

W. C.

THE LIQUATION OF GOLD AND PLATINUM ALLOYS.*

By EDWARD MATTHEY, F.S.A., F.C.S.,
Associate Royal School of Mines.

It is a well-known fact that when molten alloys of certain metals are cooled, some of the constituents separate and become concentrated either in the centre or in the external portions of the solidified mass; to this segregation the name of liquation is given. It is specially noticeable in the case of silver-copper alloys, and its importance is now being widely recognised in almost all branches of metallurgy.

In the case of gold, however, the phenomenon of liquation does not appear to have been much observed. Gold alloys, to the value of many millions sterling, pass annually from hand to hand upon the results of assays cut from the external portions of ingots, which assays cannot, of course, be trustworthy if the centre of the bars differs in composition from the external portions. Peligot has recently endeavoured to obtain evidence of liquation in gold-copper alloys, and has concluded that it does not

exist.* Roberts-Austen,† who has devoted much time to the study of liquation, has also satisfied himself that gold-silver alloys do not re-arrange themselves on cooling.‡

It is, of course, well known that gold does not retain on solidifying certain metals of the platinum group; for instance, iridium, when associated with it, always tends to fall through the fluid metal, and is found at the bottom of the solidified mass, but this is probably not a case of true rejection of a metal by liquation, but is due to the higher specific gravity of the iridium, coupled with the fact that the usual heat at which gold is melted is not sufficiently high to bring about a true alloy. It appeared to me that alloys of gold and platinum would well repay examination. They have been generally considered to be uniform in composition, but certain results which I obtained in the course of their treatment led me to suspect that they would give interesting results, and the following experiments were therefore undertaken.

The metal platinum frequently occurs in the gold and silver bullion which has to be treated by the ordinary methods of refining, and its presence occasions no small amount of trouble to the refiner.

It is well known that there are two methods of refining, both of which involve alloying one part of gold with (about) three parts by weight of silver, and treating the mass directly—

- (a). With nitric acid.
- (b). With sulphuric acid.

The final result from either method, if properly conducted, is fine gold and fine silver—that is to say, if the alloy so treated is composed of gold and silver only (a little copper present making no difference).

In the case of platinum being present in the gold or the silver, if it is refined by the nitric acid process, the platinum, when existing in small proportions, is eliminated with the silver, becoming dissolved up with it, leaving the gold free, and the platinum so dissolved can afterwards be readily separated from the silver, but upon the large scale refining by means of nitric acid is far too costly; practically, therefore, this has to be replaced by the sulphuric acid process.

In an alloy of gold and silver, containing a small proportion of platinum, nearly all the silver is dissolved by the sulphuric acid, leaving the platinum associated with the gold.

In order to simplify matters for further treatment, this partially refined gold holding the platinum is melted and assayed, to determine the amount of platinum and gold it contains; it is the platinum-gold alloys so obtained that I desire to bring under notice.

It has been found in practice that the ordinary method of assaying a small portion cut from one end of a bar or ingot of such metal does not indicate the actual percentage of gold and of platinum existing in the entire mass, and it is therefore evident that the platinum has been re-distributed by liquation during the cooling and solidification of the mass.

Having been struck by the experiments made by Professor Roberts-Austen, as detailed in the paper to which reference has already been made, I cast some gold containing platinum into a special iron mould 3 inches in diameter, and cut the spheres of metal so obtained in two halves. I may mention that I had to cast these spheres many times over in order to obtain a solid casting, so great was the shrinkage.

Portions were then carefully taken from each of the points marked on the diagrams A, B, and C given herewith, and the results of the assays of the metal taken at each point of the hemispheres are indicated on the diagrams.

- A. Composed of about 880 gold to 050 platina.
- B. Composed of about 700 gold to 120 platina.

In the one case the maximum difference between the

* *Bulletin Société d'Encouragement*, 1889, p. 481.

† *Roy. Soc. Proc.*, vol. xxiii., 1874, p. 481.

‡ "Nineteenth Annual Report of the Mint," 1888, p. 35.

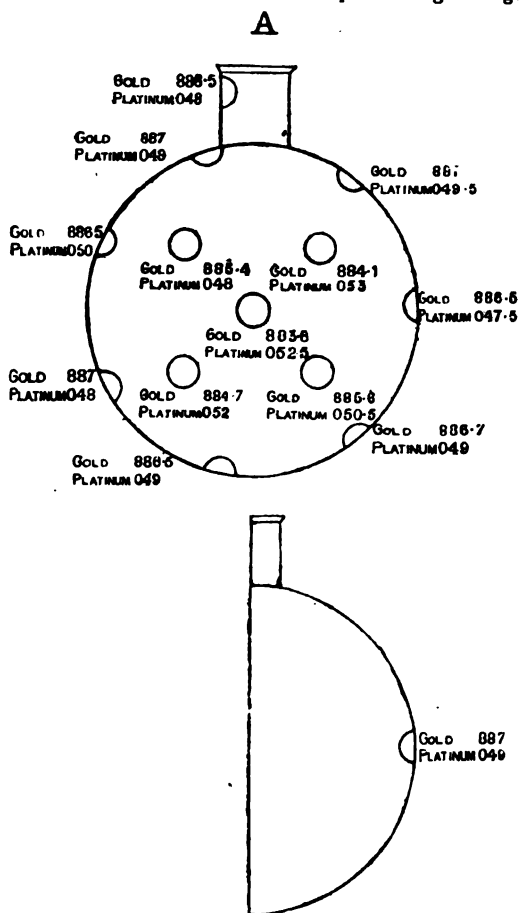
* A Paper read before the Royal Society, February 13, 1890.

gold percentage is a variation of 0.32, viz., 887 on the outside against 883.8 at the centre of the alloy; and in the platinum 0.075 on the outside against 0.525 at the centre, an extreme variation of 0.05 is shown.

In the other case the maximum difference between the gold percentage is a variation of 0.41, viz., 732.4 on the outside against 694.1 at the centre of the alloy; and in the platinum 1.22 on the outside against 1.66 at the centre, an extreme variation of 0.44.

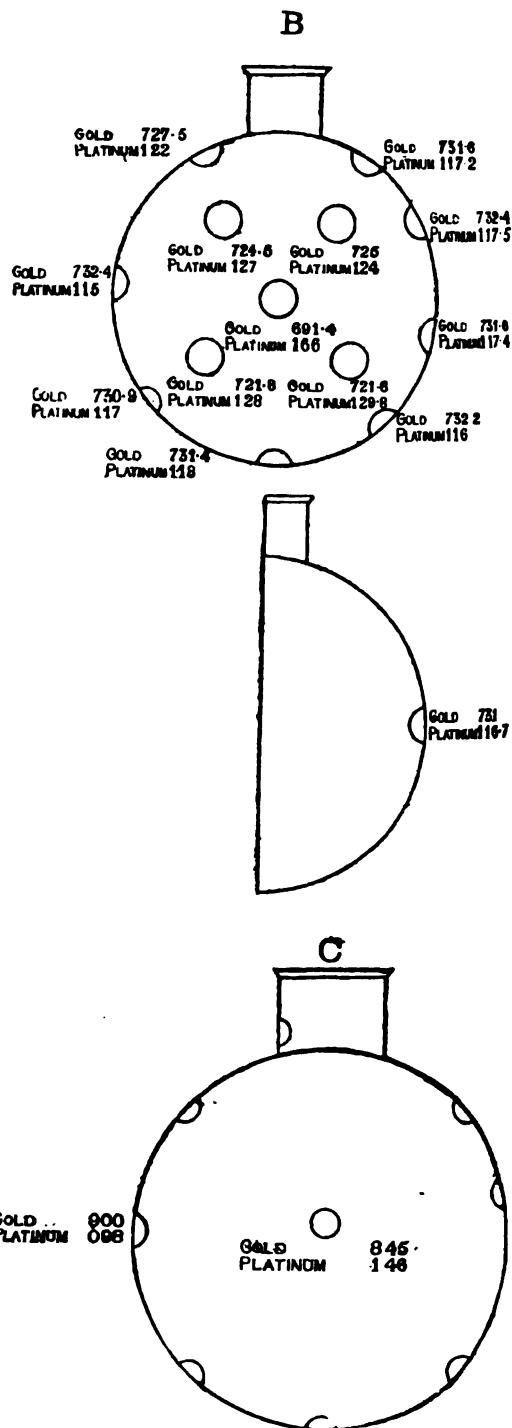
Thus showing indisputably that the platinum in cooling liquates from the gold and becomes concentrated towards the centre of the alloy.

In support of these experimental results I give the actual figures obtained from six platinum gold ingots,



taken at different times and of different qualities, as they occurred in the course of refining commercially. Each of these bars, after melting and assaying, was separately heated with a view to extract the amount of gold contained. It will be at once seen that the higher percentage of gold indicated by the assay of a portion cut from one end of the ingot is not borne out by the actual amount of fine gold obtained by refining, which, of course, truly represents the proportion of gold existing in each bar.

No.	Weight in troy ounces.	Platinum by assay.	Gold by assay.	Percentage of gold by the fine gold actually obtained.
42	728.5	0.111	0.825	0.812
67	355.0	0.120	0.660	0.630
109	589.5	0.120	0.800	0.780
126	435.0	0.045	0.850	0.845
149	480.5	0.086	0.842	0.830
168	473.0	0.110	0.830	0.821



These results prove that the percentage of gold in the outer portion of ingots of platinum gold alloy does not represent the true percentage of gold in the alloy, and that liquation does take place to an extent which, independently of its scientific and metallurgical interest,

has, I believe, been by many overlooked up to the present time in commercial transactions with such metal.

The results given were observed in platinum gold alloyed with silver, with copper, and with both silver and copper; but in order to prove whether or not such alloy had any tendency to carry the platinum to the centre of the mass, I melted 900 parts of fine gold with 100 parts of pure platinum, and, after repeated meltings, cast this alloy into the same mould used for the experiments recorded above. The result was, as in the previous cases, liquation of the platinum towards the centre of the sphere, the gold and platinum in 1000 parts being as 900 to 100 on the exterior, against 845 and 146 at the centre of the mass (see diagram C).

THE TREATISE OF DEMOCRITUS ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

(Continued from p. 102).

THE BOOK OF SILVER.

XVI. THE SURFACE OF A COPPER ALLOY IS WHITENED BY AN ARSENICAL COMPOUND.

Fix quicksilver from arsenic, or sandarach, or that thou knowest, as of custom, and mix *Venus* with iron treated with sulphur, and it will be whitened; but whitened magnesia is also excellent, and sublimed arsenic, and calcined cadmia, unfired sandarach, whitened pyrites, and ceruse roasted with sulphur. Thou dissolvest iron by throwing into magnesia, or the half of sulphur, or a little of loadstone, since that has affinity with iron. Nature rejoices with nature.

XVII. A COMPOSITION FOR AMALGAMATING THE SURFACE OF ALLOYS.

Taking the aforesaid vapour,* heat it with castor or radish oil, mixing with a little alum; then taking tin, purge it with sulphur, as of custom, or *marchasite*, or what is known to thee, and throw it into the vapour, mixing the whole. Roast, covered with coals, and thou shalt see this medicine formed, like to white lead, which whitens all (metallic) bodies,† but by anointing. Mix with it Chian earth, or Asterites, or Aphroselinum, or that thou knowest, since Aphroselinum associated with mercury whitens all (metallic) bodies. Nature conquers nature.

XVIII. THE SAME APPLIED TO ORICHALIUM ALLOY.

Take white magnesia; thou shalt whiten it with brine and alum, in sea-water, or citron juice, or with the smoke of sulphur; for the fume of sulphur, when it is white, whitens all things. But others say that the fume of cobaltia whitens it. Mix with it, after whitening, equal parts of lye, that it may become white enough. Taking of whitish bronze, of orichalium, I say, 4 ounces, place it in a crucible, placing under it little by little 1 ounce of previously purged tin, agitating until the substances unite; it will be frangible. Throw on, therefore, the half of white medicine, and it will be the chief; for whitened magnesia does not render bodies fragile, or allow the blackness of bronze to come forth. Nature restrains nature.

XIX. A WHITE ALLOY OF LEAD IS MODIFIED BY ARSENICAL COMPOUNDS.

Take the white sulphur, which will flourish whitest; but thou shalt whiten it, dissolving with urine in the sun, or alum and sea-water. Dissolve it with sandarach, or the urine of a young girl, for six days, until the medicine

nearly approaches the likeness of marble; when it becomes so, it will be wonderful, for it whitens *Venus*, softens iron, takes away the creaking of tin, renders lead white, and makes substances *infrangible*, and tinctures permanent. For sulphur mixed with sulphur makes *divine* substances, since they have close relationship with each other; for natures rejoice with natures.

XX. A WHITE ALLOY OF LEAD USED TO WHITEN THE SURFACE OF METALS.

Join whitened litharge with sulphur, or cadmia, or arsenic, or pyrites, or oxymel, lest it flow widely (be too fluid). Therefore roast it with glowing embers, furnishing the vessel with a lute. Let it be combined with roasted lime, and absorb vinegar for three days, that it may have greater power of cleansing. Apply it therefore (to the metal), when it is whiter than ceruse. Very often it will be yellow, if much fire be put under it; but if it becomes yellow it will not be of use to thee at present, for the intention is to whiten bodies with it. Heat it moderately, therefore, and mix it with every body which thou desirest to whiten. If litharge be whitened, it will be lead no longer, but it easily becomes (whitened). The nature of lead is quickly changed into many forms; for natures conquer natures.

XXI. A SILVER VARNISH FOR METALS.

Taking the crocus of Cilicia, put it into sea-water, or brine, and make a liquor in which immerse heated leaves of bronze or iron, until they are whitened to thy satisfaction. Then take a half of the medicine, rub it up with sandarach and white arsenic, or unburnt sulphur, or that thou knowest, to the consistency of wax; anoint the leaf and place it in an empty closed vessel, as of custom, and put it in a vessel where shavings are being burnt the whole day. Then, taking it away, place it in a pure liquid, and the bronze will be very white; then set to work like a craftsman; for the crocus of Cilicia whitens with sea-water, and tinges metals a yellow colour with wine. Nature rejoices with nature.

XXII. ANOTHER VARNISH.

Take white litharge, and rub it up with laurel shoots, and cimolia, and honey, and white sandarach, and let it have the consistency of scrapings (viscid). Anoint (the leaf of the metal) with half of the medicine, and warm from below, as of custom. Immerse it in the remainder of the medicine, dissolving with the water of the ash of white wood; for dissolved mixtures work well without fire. Such solutions with liquors are able to resist fire; for nature conquers nature.

XXIII. A METAL IS SILVERED BY A MERCURY COMPOUND.

Taking the prescribed vapour, rub it up with alum and misy, washing with vinegar, add to it also a little white cadmia, or magnesia or unslaked lime, that it may become a (metallic) body from another (metallic) body. Mix with the whitest honey, and make a liquid, in which immerse ignited whatever thou will, and leave it in it, the operation takes place. But let the composition have a little native sulphur, that the medicine may pervade and penetrate. Nature conquers nature.

XXIV. ANOTHER TINCTURE BY AMALGAMATION.

Take 1 ounce of arsenic, and half an ounce of nitre, and 2 ounces of the cortex of the tender little leaves of *Persia*, and half (an ounce) of salt, and 1 ounce of mulberry juice, and equal parts of scissile, rub with vinegar, or urine, or of unslaked lime of urine, until a liquid is formed. Immerse in this glowing leaves of *Venus* growing black, and thou takest away the blackness. Nature conquers nature.

Thou hast all things which are required for gold and silver, nothing is left out, nothing is wanting, except the

* Probably sublimed mercury.

† The body of a substance is its metallic state.

elevation of the vapour and of water.* But these I have omitted of purpose, seeing that I have dealt with them freely in my other writings. In this writing, farewell.

(To be continued).

OPENING UP SULPHIDES SUCH AS BOURNONITE, PROUSTITE, &c., IN A CURRENT OF AIR CHARGED WITH BROMINE.

By P. JANNASCH.

THE unpleasantness of working in a current of chlorine in the determination of sulphides induced the author to submit the action of bromine upon these minerals to a careful examination. It appeared that the diluted vapour of bromine decomposes such minerals as completely as does chlorine, if not as energetically. The process is as follows:—Air passes out of a gas-holder through a Drechsel drying cylinder charged with concentrated sulphuric acid, then through another such cylinder containing 50 c.m. (2 c.c.) of bromine; then traverses a tube of potash glass 20 c.m. in length, in which the boat with the substance is heated, and ultimately enters the usual receivers filled with a mixture of equal volumes of dilute hydrochloric acid (1 : 4) and a 10 per cent solution of tartaric acid.

In the first experiments the author made he used, for conveying the bromine, a Kipp carbonic acid apparatus. Subsequently he found the use of an air-gas holder more convenient, as the reaction proceeds more readily in a current of air. An unexpected difficulty was at first occasioned by the decomposition of the sulphur bromide which remained in the receiver as a liquid. On standing or heating in a beaker, abundance of sulphur was deposited, which required to be oxidised by a further treatment with bromine. The author did not succeed in effecting a decomposition of the sulphur bromide into sulphuric and hydrobromic acid by the addition of chlorine-water or potassium chlorate. Finally he succeeded by adding to the liquid from the receiver, in a capacious beaker, an excess of bromine, and heating it on the water-bath whilst stirring diligently. In a short time all the sulphur bromide is dissolved and the excess of bromine sufficiently driven off, whereupon the sulphuric acid is precipitated at a boiling heat with barium chloride. Next the antimony and arsenic are separated in the usual manner after the removal of the barium chloride. The portion not volatile in the current of bromine, consisting of lead, copper, and silver bromides, &c., is heated in a beaker on the water-bath with dilute nitric acid for about an hour, when lead, copper, &c., pass into solution. That this may be effected rapidly and completely, the decomposition of the original sulphide in the current of bromine is so regulated that the heat is never sufficient to melt the bromides formed. The product of the reaction is quickly dissolved away from the porcelain boat on treatment with nitric acid. If silver bromide is simultaneously present the material is carefully crushed in the liquid with a glass rod. When the nitric acid has acted long enough the insoluble matters (silver bromide, gangue, &c.) are filtered off, the acid solution is evaporated to dryness, and lead, copper, and nickel are separated as usual. The mixture of silver bromide and gangue is further digested with a dilute solution of potassium cyanide (2–4 grms. of a pure preparation), when all the silver bromide is easily and completely dissolved and separated by filtration. The filtrate is precipitated by an excess of nitric acid in a porcelain capsule, the solution is dried along with the precipitate in order to destroy small quantities of silver

cyanide if formed, the residue is afresh heated with water, some nitric acid, and bromine-water, and filtered off to be weighed.

As compared with the chlorine method, the bromine process presents decided advantages. In the first place, we have to dispose of a current of gas, the regulation of which is perfectly at command, and which does not suddenly fail in the midst of operation, a difficulty which often occurs in using an apparatus charged with blocks of chloride of lime. It is also not necessary either to arrange a special apparatus for evolving chlorine with manganese and hydrochloric acid or on every new analysis to undertake the tedious arrangement of a Winkler apparatus. A cylinder filled with bromine can always be kept at hand. The consumption of bromine is so trifling and the whole process so little offensive that there is no necessity to work under a draught-hood. It is very important that, under the conditions given, iron and zinc bromides are practically non-volatile.

The following two analyses may show the accuracy of the process.

1. Crystals of Bournonite from Neudorf in the Harz.

Pb	40.20
Cu	12.55
Sb	26.35
S	19.90
Gangue	0.50
	99.50

2. A Massive Crystalline Specimen of Pyrrargyrite from Chanarcillo in Chile.

Ag	58.42
Sb	21.10
Fe	1.33
S	18.20
Quartz	0.78
	99.83

The bromine, before use, must be tested for a possible impurity of sulphuric acid. If argentiferous sulphides are in question the bromide must be free from chlorine, so that the silver may be weighed as bromide. For this purpose a portion of the reagent is shaken up with powdered potassium bromide, let stand for some time, and the necessary quantity is filtered through slag-wool.—*Journal für Praktische Chemie.*

A NEW METHOD FOR THE ANALYSIS OF PYRITES.

By P. JANNASCH.

In executing the analysis of sulphides, previously recorded, the author made the observation that on very gently heating the substance, the portion carried away in the current of bromine contained no iron, or only traces, on account of the very slight volatility of the ferric bromide formed. This observation led to the idea of attempting to open up pyrites by heating them in fine powder in a current of bromine, thus effecting a simple and expeditious separation of the iron from the sulphur. In fact, bromine acted at once upon the material placed in a porcelain boat, and heated in a tube of potash-glass, with formation of chloride of sulphur. But at the end of the experiment the fixed residue was only in part soluble in hot hydrochloric acid, whilst another part, judging from its appearance, had remained undecomposed. A series of quantitative determinations of the sulphuric acid really formed gave an approximate result of 26 per cent of sulphur as having been liberated. Hence the pyrites had given up to the bromine only one atom of sulphur,

* This seems to point to a work on distillation, which was practised in the first centuries of our era.

leaving iron monosulphide, which, on further treatment with strong nitric acid, readily dissolved as ferric sulphate. Better results were obtained by using vapours of bromine and nitric acid conjointly for opening up the pyrites. To effect this behind the boat with the powdered pyrites there was placed another, half-filled with fuming nitric acid, and the nitric fumes are mixed with the bromine vapours by a proper management of the heat. In this manner the pyrites, very finely powdered, was completely opened up, but not without the use of a strong ignition, whereby much of the iron was volatilised. This circumstance induced the author to dispense with bromine, and work merely in a current of air containing nitric vapours. The apparatus used was arranged as follows:—

Air passes from a gas-holder through strong sulphuric acid and through a Drechsel flask containing about 50 c.c. of strong fuming nitric acid. It passes then through a tube of potash-glass laid in a short combustion furnace, and containing the boat filled with finely pulverised pyrites, and opens into a tubulated receiver charged with 100 c.c. bromine-water, to which is further attached a Peligot tube containing 40 c.c. bromine-water, and lastly a cylinder with distilled water. To begin the decomposition, a current of air (150 to 200 bubbles per minute) is passed through the apparatus, and the substance is then heated, beginning at the back. The free anterior end of the tube is heated in order to drive the sulphuric acid into the absorption vessels as fast as it is formed.

The whole course of the reaction extends to about three-quarters of an hour, and it is then let cool in a slow current of air after removing the flask containing nitric acid. If it is too strongly heated, a sublimation of sulphur ensues, which is to be avoided as far as possible.

Finally, the tube must be strongly ignited after covering the furnace with tiles, though not so strongly as to soften

drawn out with a wire hook when the tube is cold, laid in an inverted position in a flat porcelain or platinum capsule, and heated with strong hydrochloric acid on the water-bath, when the ferric oxide is quickly dissolved. The boat is then removed, cleansed with hot water and the feather of a pen, and removed; the iron solution is evaporated almost to dryness and the insoluble portion (silica, silicates, &c.) is determined. A repeated examination showed the perfect absence of sulphuric acid, and the portion of the ore insoluble in hydrochloric acid is also free from traces of undecomposed pyrites.

A continued use of this method will doubtless lead to simplifications. It will probably be found useful, when the samples contain ingredients which interfere with the use of direct solvents.—*Journal für Praktische Chemie.*

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLET, F.R.S.,

Professor of Chemistry in the University of Virginia.

(Continued from p. 105).

Fifth Series of Experiments.

In these experiments an attempt was made to determine the ratio between the weights of metallic gold and metallic silver deposited by the passage of one and the same electric current successively through solutions of the two metals. The simplicity and accuracy with which the direct weighings may be made seemed to present decided advantage, but various difficulties were encountered, and, after the expenditure of a very large amount of time and labour upon the method, it cannot be said, on the whole, to have satisfied me with its results.

Fig. 3.

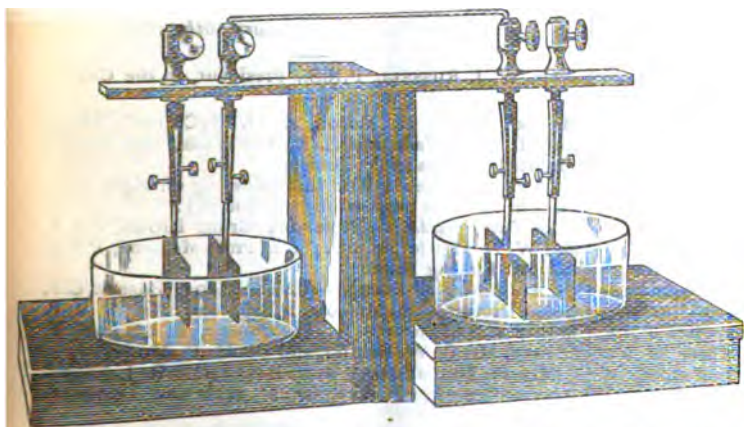
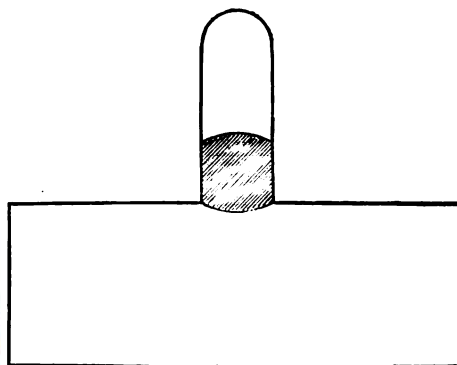


Fig. 4.



the glass tube and cause the boat to adhere. After complete decomposition the contents of the receivers are rinsed into a beaker, the excess of bromine is evaporated off, 1 c.c. of strong hydrochloric acid is added to the liquid, and the sulphuric acid is precipitated at a boiling heat with barium chloride, avoiding any considerable excess.

The precipitate, before being washed on the filter, must be very carefully purified by repeated decantation with boiling water containing hydrochloric acid, in order to remove any barium nitrate which has been carried down. A final treatment of the ignited barium sulphate with dilute hydrochloric acid and a re-weighing is recommended. If the presence of barium sulphate is to be absolutely avoided, the solution, before the addition of barium chloride, should be evaporated down in a roomy porcelain capsule. The boat with the ferric oxide is

While taking due note of the recent literature on the subject of the quantitative electro-deposition of metals from their solutions, especially the reports of work by A. Classen,⁺ Lord Rayleigh and Mrs. Sidgwick,[†] Dr. Gore,[§] Thos. Gray,^{||} and W. N. Shaw,[¶] the author of the present paper made for himself a somewhat extended preliminary examination of the effects of varying conditions on such depositions, so far at least as seemed to be required for his immediate purpose.

The general arrangement of apparatus adopted consisted of a horizontal strip, 4 m.m. thick, of vulcanite, or

* A Paper read before the Royal Society, May 9, 1889.

+ A. Classen, "Quantitative Chemische Analyse durch Electrolyse," 2te auf., Berlin, 1886.

† Phil. Trans., 1884, p. 411.

§ Nature, March 16, 1882; Feb. 1 and Feb. 15, 1883.

|| Phil. Mag., Nov., 1886, p. 389; and March, 1888, p. 179.

¶ Phil. Mag., Feb., 1887, p. 138.

hard vulcanised india-rubber, about 26 c.m. long by 3 c.m. wide, near each end of which and in the middle of the width were two small holes, through which passed short bits of brass rod, each having attached to it above a binding screw, and below a forceps-like clip, which could be opened by pressure on two little outside studs, but closed firmly, on release of this pressure, by the elasticity of the metal. In these clips were supported the plates of metal to be immersed in the electrolysed solutions, and to serve as anode and cathode terminals respectively, there being two pairs of such plates, one pair near each end of the vulcanite strip, with four corresponding binding screws. The electric current passed from the first binding screw through one of two metallic solutions—as, for instance, that containing gold—between the first pair of plates, consisting of the same metal as that in this solution, then from the second binding screw to the third (at the other end of the vulcanite strip) by a stout copper wire above, and then through the second of the two solutions—as, for instance, that of silver—between the second pair of plates, consisting again of the same metal as that in the solution in which they were immersed, thus reaching the fourth and last binding screw, the first and last binding screws being, of course, connected by wires with the terminals of the galvanic cells used to develop the current. Fig. 3 shows the disposition in question. The source of the electric current was for the most part galvanic cells of the Meidinger pattern, but in some of the experiments small Daniell cells, and also a Clamond thermo-electric battery, were used. The lower parts of the clips were heavily electroplated with the same metal as that in the solution to which they respectively belonged, in order to avoid any risk of contamination of the solution, in case there should be spluttering or accidental immersion, even for a moment, of any part of the clip.

It was decided to place the plates vertically in the liquids, but to make the vertical height small in proportion to width, so as to preserve as far as possible a uniform condition of the solution in depth. The form adopted for the plates was that of Fig. 4, the shaded part of the surface being coated with hard paraffin, with a view to preventing the strip by which the anode plate was suspended from its clip being cut across by solvent action at the surface of the liquid. This coating of paraffin was put on after the plates were first weighed, and carefully removed before the second weighing. The four plates for each experiment were of equal size as to length and breadth; in most of the experiments the immersed surface (of one side) measured about 25 square c.m., though in some cases plates of double this size were used. The thickness was the same for plates of the same metal, but those of the different metals to be compared were made to differ in thickness to such an extent as to allow for the different rate of solution to be expected of the anode plate. I was indebted to the kindness of Mr. Eckfeldt, of the Philadelphia Mint, for having plates of "proof" gold and silver specially rolled for me, with all necessary precautions as to perfect cleanliness of the rolls, &c., so as to obtain the determinate thicknesses desired.*

By heating in a Sprengel vacuum I found traces of oxygen in the rolled silver plates, and extremely minute

* Mr. Eckfeldt informed me that his method of preparing the proof silver used for these plates was as follows:—"Nitrate of silver from the gold assay parting is, after careful filtering, precipitated with hydrochloric acid, and the chloride of silver, after a thorough washing with pure water, is dried and reduced in the melting pot with pure carbonates of soda and potash and carbon in the shape of wheat flour, the melting being done in a clay crucible. The resulting silver bar is then dissolved in dilute nitric acid, and after standing some time filtered, precipitated, and reduced as before; then re-melted with the addition of pure nitrate of potash and borax. This generally gives a bar somewhat brittle (crystalline in fracture). It is then re-melted, and stirred with a pine stick, and chloride of ammonium added; when the chloride has disappeared the metal is poured. I find this method more satisfactory than any other I have tried."

traces of gas, apparently also oxygen, were likewise obtained from the gold plates, before either had been used.

The middle of the vulcanite strip was supported at a suitable height, so as to allow of equal immersion of the two pairs of plates in their respective solutions, which were contained in small vessels of good hard glass, free from lead. Care was taken to keep the vulcanite strip dry, so that there should be no practical defect of insulation between the two plates of each pair; the necessity for this precaution having been shown in some of the very early preliminary experiments with copper plates, using a wooden supporting strip; some puzzling results being traced back to a little accidental moistening with sulphate of copper solution of the part of the strip between one pair of plates, while those of the other pair were well insulated as to the strip from which they hung.

In all the experiments the two pairs of plates, previously ignited in the Sprengel vacuum, cooled, and weighed, were placed in position in the clips, the distance between the parallel surfaces of the plates of each pair being the same, and in most of the experiments measuring about 2.5 c.m., and connection was made with the terminals of the galvanic cell or cells used before immersion of the plates in the metallic solutions. All four plates were immersed at the same moment, and at the end of the experiment were in like manner lifted out of the solutions at the same moment, before the current had been broken. They were immediately introduced into one after another of several portions of distilled water, before removal from the clips, thorough washing, heating in the Sprengel vacuum, and final weighing.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 20th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MESSRS. Frank H. Mason, A. H. McConnell, Edward Russell, John Wade, and S. Russell Wells, were formally admitted Fellows of the Society.

It was announced that the following changes in the Council list were proposed by the Council:—

As *Vice-Presidents*—Professors Crum Brown, F.R.S., and W. N. Hartley, F.R.S.; *vice* Prof. McLeod, F.R.S., and Mr. Ludwig Mond.

As *Members of Council*—Messrs. Henry Bassett, C. F. Cross, Professor R. Meldola, F.R.S., and Mr. M. M. P. Muir; *vice* Professors A. H. Church, F.R.S., and F. Clowes, Mr. C. W. Heaton, and Dr. H. F. Morley.

Messrs. Bernard Dyer, R. H. Davies, and R. J. Friswell were appointed by the meeting to audit the Treasurer's accounts.

Certificates were read for the first time in favour of Messrs. William Frederick Laycock, Ph.D., 2, Park Street, Dewsbury; Arthur Sheridan Lea, Caius College, Cambridge; George Müller, 125, Mercer Street, Jersey City, N. Jersey, U.S.A.; E. H. Neville, M.A., Sidney College, Cambridge; Ernest George Scott, Mayer Hall, near Birkenhead; Willie Brewin Shuttlewood, Hong Kong; Frederick Richard M. Stone, 64, Thomas Street, Merthyr.

The following papers were read:—

10. "The Behaviour of the more Stable Oxides at High Temperatures." By G. H. BAILEY, D.Sc., Ph.D., and W. B. HOPKINS.

The authors chiefly devote attention in this notice to oxide of copper. Previous experimenters had obtained cuprous oxide by heating the oxide to redness. From the

results obtained by the authors, it appears that at higher temperatures oxygen is given off, and that an oxide having the composition Cu_2O is formed. This is insoluble in mineral acids and even in boiling aqua regia; it can, however, be changed into a soluble form by fusion with caustic potash, from which it separates on treatment with water. The oxides of lead and tin seem to behave like that of copper at high temperatures.

11. "The Influence of Different Oxides on the Decomposition of Potassium Chlorate." By G. J. FOWLER, M.Sc., and J. GRANT.

The object of the experiments has been to systematically examine the influence of the chief metallic oxides and certain unstable salts on the decomposition of potassium chlorate. Upwards of a hundred experiments have been made, the most significant of which are recorded in the paper. In each case, the temperature at which oxygen is evolved, the amount of chlorine given off, and the composition of the residue after heating have been determined. The variation of the results according to the acid or basic character of the oxide added, its physical condition, and the relative masses of the oxide and chlorate has been recorded.

The results obtained may be summarised as follows:—

(1). Acid oxides, such as V_2O_5 , WO_3 , and U_3O_8 , cause the evolution of oxygen at a reduced temperature, a metavanadate, tungstate, or uranate being formed. Chlorine is evolved in these cases in large quantity, but the whole of the oxygen of the chlorate is not evolved, as the compound of K_2O with the oxide is not decomposed either by heat or by chlorine:—



(2). Alumina probably acts similarly but less energetically, the attraction between the K_2O and Al_2O_3 not being so great.

(3). In the case of chromium sesquioxide, the oxygen is evolved at a reduced temperature, accompanied by chlorine. The decomposition may be supposed to be brought about by the affinity of the Cr_2O_3 for O, and the affinity of the CrO_3 thus formed for K_2O ; but all the oxygen of the chlorate is not evolved, since—



(4). In the case of the sesquioxides of iron, cobalt, and nickel, cupric oxide, and manganese dioxide, oxygen is evolved at a comparatively low temperature accompanied by only a little chlorine; the oxide is left but little altered at the end of the experiment.

Accepting McLeod's theory of the action of manganese dioxide (*Chem. Soc. Trans.*, 1889, 184), which is fully in harmony with the results of the experiments under consideration, it would seem that manganese dioxide first acts by reason of its affinity for oxygen and the affinity of the higher oxide thus formed for K_2O . The permanganate first formed, however, is unstable (here there is a difference between the oxides of this class and those of the preceding), and is resolved into $\text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$. The K_2MnO_4 is decomposed by chlorine into KCl and MnO_2 , which is thus regenerated. The addition of sodium carbonate retards the evolution of oxygen, probably because the manganate is thereby rendered more stable. The action of the other oxides (*cf.* Spring and Prost) of this class can, it is believed, be explained in a similar manner to that of manganese dioxide.

(5). The monoxides of barium, calcium, and lead cause no evolution of oxygen when heated with chlorate, but the latter breaks up below its normal temperature of decomposition, potassium chloride, and a peroxide being formed. Here the affinity of the oxide for oxygen induces change.

(6). On the other hand, potassium chlorate may act as a reducing agent in the presence of such oxides as silver oxide and the peroxides of barium and lead, a perchlorate being formed. No oxygen is evolved. Here the change is brought about by the affinity of the chlorate for oxygen.

In the case of the oxides of calcium, barium, and lead, the extent to which the chlorate is oxidised evidently depends on the relative masses of the interacting substances.

(7). Water of hydration appears to diminish the activity of an oxide, owing doubtless to the absorption of heat necessary for its conversion into steam.

(8). The physical condition of the oxide is of influence. Copper oxide prepared in the dry way is almost inactive.

(9). Certain substances, although apparently they undergo no chemical change, assist the decomposition, *e.g.*, powdered glass, sand, and kaolin.

(10). Oxides such as those of zinc and magnesium are inactive.

DISCUSSION.

Dr. HODGKINSON said that he had noticed that all the chlorine was expelled from potassium chlorate by heating it with either uranic or tungstic or vanadic oxide—was this because these oxides expel the chlorine from chlorides? In the case of stannic oxide, everything depended on the state of the oxide: the native form had no action, but metastannic acid expelled chlorine.

Professor McLEOD thought that the decomposition of potassium chlorate was promoted in some cases by a mere action of presence similar to that which charcoal exercises on the boiling of water: for instance, platinum black appeared to act in this way, and probably basic oxides exercised a similar influence.

Professor RAMSAY expressed the opinion that in some cases the oxides were converted into corresponding chlorates: that copper oxide, for instance, became converted into copper chlorate, which was thereupon resolved into copper oxide and an unstable oxide of chlorine; it was desirable from this point of view to study the behaviour of various chlorates.

Professor THORPE said that much had already been done in the direction suggested by Professor Ramsay; but difficulty arose as many chlorates were hydrated salts which decomposed during dehydration. After calling attention to Teed's and Frankland and Dingwall's experiments, he said there was no evidence that when, for example, manganese dioxide was used manganese chlorate was formed. Mr. Eccles had several years ago made experiments in his laboratory to test this point, and had found that no alkali was formed when manganese dioxide was used, as must have been the case if any chlorate of the oxide were produced. The non-production of perchlorate was the most remarkable feature of the change in presence of manganese dioxide (*cf. Chem. Soc. Journ.*, 1876, 856).

In reply to a remark by Professor Ramsay, Professor McLEOD said that the formation of permanganate accounted for the fact that no alkali was obtained, although chlorine was given off.

12. "The Interaction of Hypochlorites and Ammonium Salts. Ammonium Hypochlorite." By C. F. CROSS and E. J. BEVAN.

No mention is made of ammonium hypochlorite in the later text-books and dictionaries; in the last edition of "Gmelin" (vol. ii., 479), however, there is a short paragraph headed "Ammonium Hypochlorite?" in which its probable existence is spoken of on the authority of Schönbein. This chemist observed that a pungent odour is developed when ammonia is added to chlorine-water, and that the liquid exhibits bleaching powers and the property of decomposing hydrogen peroxide with liberation of oxygen; hence it was supposed that the destructive action of chlorine on ammonia is preceded by the formation of ammonium hypochlorite.

The authors have recently had occasion to study the subject more closely. On treating a dilute solution of bleaching powder with the equivalent quantity of an ammonium salt, no sensible loss of "available chlorine" takes place provided interaction occur at a low temperature (10°). The pungent odour already mentioned as noticed

by Schönbein suggested that the resulting compound was volatile, and, therefore, in order to obtain evidence as to its composition, a current of air was passed through the solution and subsequently through water and through a solution of potassium iodide acidified with normal acid; eventually the liberated iodine was titrated with thio-sulphate and the excess of acid was determined in the same solution by means of normal alkali. The iodine liberated was taken as equivalent to the chlorine, and the amount of acid saturated as equivalent to ammonia; the results obtained were—

(1). Cl = 0.0365	NH ₄ = 0.0090	2.06:1
(2). Cl = 0.0316	NH ₄ = 0.0081	1.98:1

These correspond with the formula NH₄OCl, in which the ratio of oxidising chlorine to ammonia is that of 2Cl: NH₄. Further evidence as to the composition of the compound was obtained by extracting the aqueous solution with ether, and after diluting the extract with alcohol, adding potassium iodide and the necessary quantity of thio-sulphate: the resulting mixture was neutral. The compound was also volatilised by means of a current of air, which was then washed and passed into a solution of sodium sulphite; the oxidation of the sulphite was the only change observed, the solution remaining neutral, whereas had no ammonia been present it would necessarily have become acid.

The evidence of the formation and existence of ammonium hypochlorite in solution would seem, therefore, to be complete; the isolation of such a compound, however, is necessarily attended with considerable difficulty, and all attempts in this direction have hitherto failed to give a result.

At ordinary temperatures solutions prepared as described containing from 1 to 2 grms. Cl per 100 lose oxidising chlorine comparatively rapidly; thus one containing 1.6 grms. per 100 immediately after preparation contained after filtering and standing two hours 0.12 gm.; after forty-eight hours 0.06, and after seventy-two hours 0.04.

The ammonia product presents curious anomalies in oxidising properties in comparison with other hypochlorites; thus it is without action on many colouring matters, e.g., those of vegetable fibres; a solution tinged with a drop of a solution of indigo sulphonate retains its colour for some hours, although it at once liberates iodine from potassium iodide; and it does not peroxidise hydrated lead oxide, nor does it oxidise potassium ferrocyanide in presence of acetic acid. But it oxidises sulphites and arsenites, and its effect on aniline salts is identical with that of ordinary hypochlorites.

The compound is easily formed by the electrolysis of ammonium chloride solutions.

DISCUSSION.

Professor RAMSAY said that a few months ago he also had attempted to prepare ammonium hypochlorite, and had found that on adding ammonia to hypochlorous acid nitrogen was not given off. It was to be noted that the formula of ammonium hypochlorite was equivalent to that of hydroxylamine hydrochloride.

In answer to Professor Dunstan, Mr. CROSS said that the addition of acid did not alter the properties of the liquid as an oxidising agent.

Dr. ARMSTRONG suggested that probably the authors were dealing with a chlorinated derivative of ammonia, e.g., NH₂Cl: Gattermann's experiments show that such compounds are more stable than is usually supposed.

13. "The Action of Phosphoric Anhydride on Stearic Acid." By F. STANLEY KIPPING, Ph.D., D.Sc., Heriot Watt college.

It is stated in both editions of "Beilstein" that when stearic acid is heated with phosphoric anhydride it yields a compound of the formula C₁₈H₃₄O, melting at 54—56°, insoluble in potash. As the formation of a compound so

related to the acid in this manner appeared remarkable, being, I believe, without a parallel, I have re-examined the subject, and am led to give a brief account of my results in order to reserve the study of this and similar changes.

If stearic acid be heated at about 200° in an oil-bath, and about an equal weight of phosphoric anhydride be added in small portions at a time, the whole being well stirred, a considerable quantity of gas is evolved and a black, tarry mass is obtained. The mixture is allowed to cool, then stirred with water, and the whole boiled for some time with a large excess of moderately concentrated potash in order to remove the phosphoric acid. A dark brown, almost black oil collects on the surface, and, on cooling, solidifies to a soft waxy cake; this product is separated from the alkaline solution, washed with water, transferred to a flask, and repeatedly extracted with boiling dilute alcohol. The alcoholic extracts deposit, on cooling, a yellowish flocculent substance, and there remains in the flask a dark brown waxy mass which is very sparingly soluble in dilute alcohol; this residue is being investigated.

The compound which separates from the alcoholic solution can be obtained in a colourless condition by repeatedly re-crystallising it from alcohol and ether. It crystallises in colourless waxy microscopic plates, and is only sparingly soluble in cold ether and alcohol, but much more readily in the warm solvents and in benzene; it seems to be insoluble in hot potash or in ammonia. When heated slowly in a capillary tube it begins to soften at 73° and melts completely at 75—76°, or about 3° higher than stearic acid. On combustion, 0.1420 gm. gave 0.4316 gm. CO₂ and 0.1771 gm. H₂O.

C ₁₈ H ₃₄ O.	C ₁₈ H ₃₆ O ₂ .	C ₁₈ H ₃₈ O.	Found.
C = 81.20	76.27	83.00	82.88 per cent
H = 12.78	12.68	13.83	13.85 "
O = 6.02	11.05	3.17	3.27 "

The results show clearly that the compound is not simply unchanged stearic acid, a fact which is further proved by the higher melting-point, and that it has not the composition C₁₈H₃₄O is apparent from the high percentage of hydrogen which it contains. The results of the analysis agree very closely with the formula C₁₇H₃₃O, and the experiment described below confirms this conclusion.

It seems, then, that when stearic acid is heated with phosphoric anhydride, under the conditions described above, one of the products is stearone, and that action takes place according to the equation:—



Quantitative experiments have not yet been made, but the yield appears to be as good, or better, than that obtained in preparing stearone by the distillation of salts of stearic acid.

Stearone has been previously prepared by Heintz (*Jahresb.*, 1855, 515, 516) by distilling stearic acid alone or with lime; Heintz gives 87.8° as the melting-point, whereas the compound obtained as described above melts at 75—76°. The cause of this difference has not yet been ascertained, but it is probably due to the presence of impurities too small in quantity to have any effect on the analysis. The stearic acid employed melted at about 62°; the experiments will be repeated with the pure acid.

Stearonehydroxime (C₁₇H₃₃)₂C:N·ON. A small quantity of the colourless crystalline compound (m. p. 75—76°) was dissolved in warm alcohol and boiled for about three hours with excess of hydroxylamine and a large excess of potash. On cooling the solution and adding water, a colourless flocculent substance was precipitated; the solution was filtered, the precipitate washed repeatedly, first with dilute hydrochloric acid and then with water, and dried on a porous plate. 0.2514 gm. gave 6.6 c.c. of nitrogen at 755 m.m. and 40°, or 2.67 per cent; the theoretical percentage corresponding to the

formula $C_{35}H_{71}NO$ is 3.07 per cent. This hydroxime is a colourless, seemingly amorphous compound readily soluble in benzene and warm alcohol, but insoluble in acids and in alkalis. When heated very slowly in a capillary tube, it begins to soften at about 53° , and melts completely at $58-59^{\circ}$. It separates from alcohol as a powder which, when examined under the microscope, appears to be perfectly homogeneous.

14. "Semithiocarbasides." By AUGUSTUS E. DIXON, M.D.

Orthotolylphenylsemithiocarbaside (from *o*-tolylthiocarbamide and phenylhydrazine) forms vitreous prisms melting at $162-163^{\circ}$. It is nearly insoluble in water; soluble in alcohol, ether, and chloroform.

Phenylorthotolylsemithiocarbaside (from phenylthiocarbimide and *o*-tolylhydrazine) is isomeric with the preceding. It forms long, pearly-white prisms melting at $145-146^{\circ}$; it is nearly insoluble in water, but dissolves freely in alcohol, ether, and chloroform.

Methylphenylsemithiocarbaside forms delicate, silky needles melting between 88° and 89° . It is somewhat soluble in hot water; very soluble in alcohol and in chloroform.

Ethylorthotolylsemithiocarbaside crystallises from alcohol, in which it is rather freely soluble, in fine white needles possessing a faint pink tinge. It melts at $129-130^{\circ}$; is insoluble in cold water, but dissolves freely in ether and chloroform.

Allylphenylsemithiocarbaside separates from benzene in tangled masses of silvery-white flexible needles, which become highly electrical on friction; it melts at $118-119^{\circ}$ to a bluish green liquid. It is soluble in ordinary solvents, but is precipitated from solution in benzene by light petroleum.

These compounds all give with concentrated sulphuric acid solutions varying in colour from greenish-blue to deep azure. They are desulphurised, either with great difficulty, or not at all, by boiling alkaline lead tartrate; but readily yield their sulphur to ammoniacal silver nitrate. With $CuSO_4$ or Fe_2Cl_6 they afford strongly marked colour changes.

The connection between the solubility and fusibility of the several compounds is traced, and it is shown that, as a rule, Carnelley's principle holds good that the greater the solubility the lower is the melting-point; the author also suggests an application of Carnelley's principle to connect the melting-points with the molecular structure.

15. "Note on the Production of Ozone by Flames." By J. TUDOR CUNDALL, B.Sc., University College, Cardiff.

It is stated by L. Ilosvay de N. Ilosva (*Ber. Referate*, 1889, 791 *et seq*) that when the products of combustion of various kinds of flames are collected, they do not exhibit the smell and taste of ozone. This is confirmed by the results of some unpublished experiments made by the author in a similar manner in 1886.

Recently, however, the author has found that the air aspirated through a tube (3 m.m. in bore) whose mouth is fixed about 5 m.m. above the tube, and 5 m.m. away from the flame, of a Bunsen burner, both tastes and smells strongly of ozone. Similar results were obtained both from luminous and hydrogen flames.

It was not found possible to confirm this fact by any other test for ozone, owing to the impossibility of finding any which was sufficiently sensitive which was not common to it and dilute nitrogen oxides. At first sight it seemed that Houzeau's papers (impregnated with red litmus and potassium iodide) would give the necessary distinction, as an acid gas could not be expected to give an alkaline product. Ilosva states, however, that nitrogen oxides turn these papers blue, and the author has confirmed this result.

Papers impregnated with thallium hydroxide were employed with negative results, but, on testing them in a stream of ozonised oxygen from a Siemens tube, they were found to be far from sensitive. The same applies

to an acidified solution of sulphanilic acid and α -naphthylamine, which certainly gives a yellow colour with a fair amount of ozone, but this colour is completely masked by the rose-red produced by small traces of nitrogen oxides which may be present simultaneously.

The gas aspirated in this way both from coal-gas and hydrogen flames gave definite indications with mercury of the peculiar behaviour of ozone, but the quantity present was not sufficient to make the mercury adhere completely to its containing flask.

In conclusion, the author agrees with Ilosva in so far that he regards the smell and taste of ozone as the only tests for it that are at all reliable when it is present only in traces, but differs from him as regards its formation in flames; although nitrogen oxides are undoubtedly formed in flames, yet at the same time ozone can be detected by aspirating the air surrounding the flame in such a manner as to get a minimum of the products of combustion, and at as low a temperature as possible.

Anniversary Meeting.

The anniversary meeting will be held at Four o'clock in the Afternoon of Thursday, March 27.

It is arranged that, in the evening of the same day, the Fellows and their friends will dine together at the Whitehall Rooms, Hôtel Métropole (entrance in Whitehall Place). Dinner will be on the table at seven for half-past seven o'clock. Fellows intending to be present are particularly requested to give notice by means of a post-card which they will receive for the purpose not later than Saturday, March 22. Price of dinner, including wine, one guinea.

It is proposed to hold a special meeting of the Society on Thursday, May 8, for the exhibition of new interesting apparatus or specimens. Fellows who desire to exhibit objects are requested to communicate with the Secretaries.

At the Meeting on March 20 Professor Judd, F.R.S., will deliver a lecture on "The Evidence afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressures."

CORRESPONDENCE.

LARD.

To the Editor of the Chemical News.

SIR,—When I replied to the letter of Mr. John H. Swindells, Ph.D., I did not do so in the spirit of rhodomontade, which characterised his remarks on the above subject. I simply stated facts, being surprised that anyone should express such incredulity about the purity of an article of food which, from pretty long experience, I was certain was, as a rule, sold in sweet, fresh, and pure condition. Dr. Swindells says he was not referring to the use of stearin, the only matter which I think could "not be considered an adulteration." Anyone would know that starch, lime, and cotton, or sesame oils, when added to lard, are adulterants. Starch and water, tradition says, were, before the advent of Food and Drug Acts, added in considerable quantity to lard. But I will not dwell upon the past; I shall confine myself to my own experience. In the first place, the addition of stearin to lard is a necessity, and, being so, it is only folly to prejudice its use by calling it "doctored dripping." During the last fifteen years I have examined almost every registered brand of lard made in England, but I have never found a trace of starch or lime in one. I have found cotton-seed oil in lard sold as compounds, I have found 20 per cent of water in lard sold as "prime watered lard," I have found from 2 to 5 per cent of water occasionally in some samples, and I have found infinitesimal particles of b-

stearate of soda, the result, not of adulteration, but of careless refining. I have also found samples rancid from age or causes beyond my knowledge. On the whole, however, the lard which I have examined has been, as a rule, pure, sweet, and wholesome, showing that the refiners of England endeavour to supply a good article.

If only the kidney-fat of the hog is to be called lard, Dr. Swindells is certainly right when he says "something must be wrong." But this is only an Utopian idea, as from time immemorial the whole of the fat enveloped by the adipose tissue of the hog has been, when rendered down, called lard, and sold as such in all the markets of the world. Had mankind to depend for their supply of lard solely upon what is derived from the kidney-fat of the hog, the majority of the human race would, I think, have little chance of procuring it. In conclusion, I beg to thank you for the space you have allowed me to pass my opinion on this subject.—I am, &c.,

WILLIAM BROWN.

3, Hereford Road, Seaforth,
Liverpool, March 5, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTES.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 6, February 10, 1890.

Bodies which Present a Tension of Dissociation Equal to the Vapour-Tension of their Saturated Solutions.—H. Lescaur.—The class of saline hydrates presents numerous examples of this class of bodies. This feature is by no means an anomaly, but belongs to all saline hydrates during a longer or shorter period of their definite existence.

Action of Fluorine on the Different Forms of Carbon.—H. Moissan.—Fluorine, unlike chlorine, is able to combine directly with carbon. If dry, cold lampblack, not ignited and freed from carbides by treatment with petroleum and boiling alcohol, is placed in a current of pure fluorine, there is an immediate combination accompanied with incandescence. Charcoal of light woods, under the same conditions, may also take fire spontaneously. If the density of the charcoal is greater, and if it is free from dust, its temperature must be raised to 50° or 100° before incandescence takes place. Ferruginous graphite from cast-iron requires to be raised to a heat below dull redness before it can combine with fluorine. The graphite of Ceylon, purified with melting potassa, takes fire only at a rather higher temperature. Retort-coke does not combine until raised to redness. The diamond, kept at a red heat in the flame of a Bunsen burner, suffers no change of weight in a current of fluorine. If fluorine is passed over carbon which is readily attackable without raising the temperature too high, there is produced a gaseous mixture consisting chiefly of carbon tetrafluoride, a colourless gas which liquefies at 10° under a pressure of five atmospheres. If fluorine is passed over an excess of charcoal heated to redness there is formed another gaseous body which liquefies at 10° under a pressure of nineteen to twenty atmospheres. The two fluorides give a very extended spectrum of lines and bands, in which the rays of fluorine are very distinct.

A General Method of Preparing Carbon Fluorides.—C. Chabré.—The author heats in a tube of Bohemian glass, sealed at the lamp, 5 grms. silver fluoride with 1.55 grms. carbon chloride (CCl₄) to 220° for two hours.

The Blue Flame of Common Salt and the Spectral Reaction of Copper Chloride.—G. Salet.—The spec-

trum of the flame of salt thrown on a coal fire has been described by Mr. A. P. Smith in the *CHEMICAL NEWS* (1879, p. 141). Its bands are due to copper chloride. Copper may be detected as follows in the ash of the coke or the coal employed. The metals present are dissolved in the ordinary manner and the copper is precipitated on a steel needle. This needle, if placed in the outer flame of a Bunsen burner, does not colour the flame, but if a little hydrochloric acid is volatilised in it there is at once seen a fine blue colouration, giving the spectrum of copper chloride. To chlorinise a flame, as it is often needful in spectrum analysis, the most convenient way is to introduce into it a bundle of some thirty very fine platinum wires moistened with hydrochloric acid.

The Electric Resistance of Iron and its Alloys at High Temperatures.—H. Le Chatelier.—The author's results are given in the form of a diagram.

Thermo-Chemical Researches on Silk.—Leo Vignon.—The absorbent power of silk is shown in the calorimeter by distinctly appreciable liberations of heat. These liberations represent the sum of the chemical and physical work effected by the contact of the silk with the reagents.

Determination of Potassa and Humus in Soils.—J. Raulin.—This paper will be inserted in full.

Colouring-Matter of the Diaptomes.—R. Blanchard.—The Copepods of the genus *Diaptomus* are represented in the lakes of the high Alpine tablelands by the species *D. bacillifer* and *D. denticornis*. They vary in colour from carmine-red to white, colourless, or even to a pale greenish blue. Their pigment is a carotene, an additional substance common to animals and plants. This proves that the animal organism is able to produce hydrocarbides, bodies hitherto unknown in healthy animals, though very common among plants. This is a new example of the existence of carotene independently of chlorophyll.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., No. 12.

Easy Processes for Distinguishing Phosphorus Oxychloride and Trichloride.—G. Denigès.—A very small quantity of zinc powder is put in a very dry glass tube and a few drops of the liquid in question is poured upon it. The trichloride is without sensible action, whilst, with the oxychloride, there is immediately a brisk reaction. The grey zinc-powder turns to a dirty green, then to a yellow. If water is added, with agitation, the zinc dissolves in the case of the trichloride, forming a liquid almost colourless. With the oxychloride the oxide P₄O remains unchanged and the colour of the liquid is darkened.

Synthesis of Certain Seleniuretted Compounds in the Aromatic Series.—C. Chabré.—The author has studied the reaction of selenium tetrachloride alone upon benzene; the same reaction in presence of aluminium chloride; the behaviour of selenium with organo-metallic compounds; the formation of phenyl selenide; the reaction of oxidisers upon phenyl selenide; the action of selenious anhydride and of selenious acid upon benzene; the synthesis of oxygenous selenium compounds; the action of bromine-water upon diphenyl-selenine; the action of selenious anhydride upon the amines; the formation of melted selenious anhydride; the reduction of selenious acid by alcoholic fermentation. In order to determine selenium the author attacks the products at 220–240° in a sealed tube with forty times their weight of pure nitric acid. He then dilutes with water, neutralises with potassa, and, after evaporation and the addition of a large quantity of hydrochloric acid, precipitates the selenium with sodium bisulphite.

The Vapour-Density of Selenium Chlorides.—C. Chabré.—The experimental densities are 7.69 and 8.123, the theoretic value being 7.95.

MISCELLANEOUS.

The Mining and Metallurgical Exhibition.—On July 2 there will open, at the Crystal Palace, an Exhibition of novel and important kind. Mining and metallurgy rank among our most important and most progressive industries, and an exhibition dealing exclusively with their leading features will present a very high interest. Among the regulations for exhibitors we notice as especially important that nothing of an explosive, inflammable, or dangerous character will be admitted, and that the articles displayed will be at the exhibitor's own risk in all respects. It is not the intention of the Executive Council to issue awards and medals indiscriminately, though they "will initiate special competitions of mining and allied machinery, and make special awards in these and other cases, as may be decided upon by any jurors who may be appointed." This passage of the prospectus is scarcely as definite as we should wish to see. Probably the entire absence of awards and medals would have been a better policy. A series of popular and technical lectures will be delivered on the subjects of the Exhibition and a mining congress is also announced. An important feature is that one-half the certified surplus will be distributed among the exhibitors in proportion to the space which they have paid for and occupied. The other half will be disposed of by the Council "either in founding a scholarship at the Royal School of Mines, or in helping some other institution connected with mining and metallurgy. Applications for space must be sent in to 18, Finch Lane, not later than March 15. The articles admissible will fall within the following range:—Machinery in motion and at rest; gold-mining; silver-mining; diamond-mining; iron stone and ore mining, with the manufacture of iron and steel; lead mining and manufacture with the production of white-lead; tin-mining and smelting, with the manufacture of tin plate; copper-mining, smelting, and refining; coal-mining, with coke, coal-gas, and utilisation of the by-products; the petroleum and asphalt industries; mining for precious stones; the salt industry; mining for antimony, mercury, arsenic, manganese, cobalt, platinum, bismuth, uranium, &c., ochres, sulphur, and other minerals; manufacture and uses of alloys; nitrates and phosphates; assaying and chemistry of mining and metallurgy, quarrying, cements, clays, concretes; electricity applied in mining and metallurgy; explosives (*shown in model only*) used in mining; scientific instruments used in mining; collections of minerals; mining and metallurgical literature; tools and appliances; ambulance practice and condition of working miners. A guarantee fund has been subscribed to the amount of £2410 6s. The sum total of all calls made upon the guarantors will be repaid to them out of the first funds available after payment of expenses. The project seems a departure from the common run of exhibitions; it merits and will, we trust, command success.

Royal Institution of Great Britain.—The following are the arrangements for the Lectures after Easter:—

The Hon. George C. Brodrick, D.C.L., Warden of Merton College, Oxford, three Lectures on "The Place of Oxford University in English History"; on Tuesdays, April 15, 22, 29.

Louis Fagan, Assistant Keeper of Prints and Drawings, British Museum, three Lectures on "The Art of Engraving": (1) Line Engraving; (2) Wood Engraving; (3) Mezzotint Engraving; on Tuesdays, May 6, 13, 20.

Andrew Lang, three Lectures on "The Natural History of Society"; on Tuesdays, May 27, June 3, 10.

C. V. Boys, A.R.S.M., F.R.S., Assistant Professor of Physics, Normal School of Science, South Kensington, three Lectures on "The Heat of the Moon and Stars" (the Tyndall Lectures); on Thursdays, April 17, 24, May 1.

Professor Dewar, M.A., F.R.S., Fullerian Professor of Chemistry, R.I., Jacksonian Professor of Natural Ex-

perimental Philosophy, Cambridge, six Lectures on "Flame and Explosives"; on Thursdays, May 8, 15, 22, 29, June 5, 12.

Captain W. de W. Abney, R.E., C.B., F.R.S., three Lectures on "Colour and its Chemical Action"; on Saturdays, April 19, 26, May 3.

Charles Waldstein, Litt.D., Ph.D., three Lectures on "Excavating in Greece"; on Saturdays, May 10, 17, 24.

The Rev. S. Baring-Gould, M.A., three Lectures on "The Ballad Music of the West of England" (with Musical Illustrations); on Saturdays, May 31, June 7, 14.

New Process for Titrating Alcohol with Chromic Acid.—R. Bourcart.—In the author's process the diluted alcohol is heated with dilute solutions of potassium bichromate and sulphuric acid and gradually oxidised, first to aldehyd and then to acetic acid. The conversion is quantitative. As it is easily seen, $\frac{1}{2}$ mol. of bichromate are required for the oxidation of 1 mol. alcohol. The author operates in tubes sealed at both ends, or in a tube sealed at one end and closed at the other with a caoutchouc stopper, the end of which is secured in any convenient manner. After being heated for two to three hours in a boiling water-bath the tube is let cool. The liquid is then mixed with a sufficiency of potassium iodide, so that the iodine set free may re-dissolve, and titrated with hyposulphite until the colour passes from a dirty yellow to a yellowish green. Starch-paste is then added, and the titration is continued until the dark violet colour disappears. The liquid does not become colourless, as it is coloured a turquoise blue by chrome-alum, which, however, does not interfere with the sharpness of the reaction. The author uses a solution of bichromate containing exactly 5 grms. per litre (in some cases, also, a 1 per cent solution), a sulphuric acid of 25 vol. per cent (in some cases 10 per cent), a 10 per cent potassium iodide solution, and a 2 per cent solution of starch which has been boiled and filtered. The solutions of alcohol taken for examination are of about 0.5 per cent. To 10 c.c. of such dilute alcohol there are used about 50 c.c. of the 0.5 per cent solution of bichromate and 10 c.c. of the 25 per cent sulphuric acid.—*Bull. Soc. Ind. de Mulhouse and Chemiker Zeitung.*

Determination of Silicon in Crude Iron and in Spiegeleisen.—M. Clerc.—The author places in a flask holding from 350 to 400 c.c. 4 grms. of the metal as finely pulverised as possible, along with 15–20 c.c. of water, 8–10 c.c. of pure bromine, and 75 c.c. of pure hydrochloric acid, and heat to about 100° on the sand-bath. The silicon is oxidised and the iron and manganese pass into solution. If the heating is continued until the volume of the liquid is reduced to 40–50 c.c., the process is completed. The liquid is diluted with 200–300 c.c. hot water, filtered, and the insoluble residue is incinerated, when the silica is obtained white and pure. The error does not exceed 0.001–0.002 per cent.—*Soc. de l'Ind. Minérale and Chemiker Zeitung.*

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Laboratory and Lecture Room Fittings.—Will any reader of the CHEM. NEWS recommend a firm to carry out above-mentioned work? Good work at a fair price required.—BALBUS.

Analysis of Manufactured Rubber.—In what way or process can I determine the composition of manufactured rubber, so that I might know what quantity of the different compositions are used?—ANALYST.

Fire-damp Indicator.—Could any of your readers inform me whether there is an effective instrument for indicating explosive gas in coal mines, and if it is in general use in dangerous pits?—A. L. C.

ERRATUM.—Page 109, column 1, line 17 from top, or "sulphate read "phosphate."

MEETINGS FOR THE WEEK.

- MONDAY, 10th.—Medical, 8.30.
 TUESDAY, 11th.—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
 — Society of Arts, 8. "The Claims of the British School of Painting to a Thorough Representation in the National Gallery," by James Orrock, R.I.
 — Institute of Civil Engineers, 8.
 — Photographic, 8.
 — Royal Medical and Chirurgical, 8.30.
 WEDNESDAY, 12th.—Society of Arts, 8. "The Chemin de fer Glissant, or Sliding Railway," by Sir Douglas Galton, K.C.B., D.C.L., F.R.S.
 — Geological, 8.
 — Microscopical, 8.
 — Pharmaceutical, 8.
 THURSDAY, 13th.—Royal, 4.30.
 — Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
 — Mathematical, 8.
 — Institute of Electrical Engineers, 8.
 — Society of Arts, 5. "Agriculture and the State in India," by W. R. Robertson.
 FRIDAY, 14th.—Royal Institution, 9. "The Glow of Phosphorus," by Prof. T. E. Thorpe, Ph.D., F.R.S.
 — Astronomical, 8.
 — Quekett Club, 8.
 SATURDAY, 15th.—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
 — Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1581.

THE SYSTEM OF "SEALED PAPERS."

IN reply to the strictures on this practice urged by Mr. Crookes in his Presidential Address before the Chemical Society in March, 1889, M. Lecoq de Boisbaudran utters a vehement protest. The distinguished French chemist is in error if he supposes that he was here personally or specially alluded to. A Presidential Address before the Chemical Society consists of two portions, having, in reality, no connection beyond their being delivered on the same occasion. In the former of these portions the practice of "sealed papers" was made the subject of condemnatory mention. But this has not the least reference to the second, or scientific portion of the Address, in which are discussed the views of M. de Boisbaudran on the rare earths.

No one can deny that "sealed papers" do lend themselves to dishonourable, if not formally dishonest, practices; and, as the German proverb says, "opportunity makes thieves." The *savant* who deposits half a dozen sealed papers with some learned society calls for one of them only to be opened. What was in the others the world never learns. Why are they not also opened and read, unless they contain something which the author desires to conceal, i.e., some different and contrary solution of the question concerned? If the suppressed papers are merely steps leading up to the conclusion ultimately adopted, we fail to see the motive for withholding them from ultimate inspection. The advantage gained by the dishonest person whom Mr. Crookes supposes is distinctly that of priority—and in many cases that is everything. That the person injured—the true discoverer—"cannot have gathered his ideas from the contents of the sealed paper" is perfectly true and very unimportant. No one says he has!

M. de Boisbaudran's objections to the publication of preliminary papers, as customary in England and Germany, are not valid. The subjects which a chemist thus appropriates for his further study are not "vast questions," but are generally well defined in their scope, as anyone may see who will look over the "preliminary notices" published in various scientific journals. Nor will they be found to be "hazardous hypotheses." By speaking of some imaginary "conscientious experimentalist," whose "useful researches" are thus interfered with, M. de Boisbaudran evidently insinuates that the authors of such notices are not conscientious, but "dishonest, or simply superficial," and that they "effect no real work." But the writers thus disparaged are not like the dealers in "sealed papers," working under a cloak. Their memoirs come at once under the notice of their colleagues, and if they are found to be dishonest or superficial, or if they are not worked to some definite conclusion, they speedily find their own level.

It must not be supposed that the objection to "sealed papers" is a peculiarity of Mr. Crookes. When attempts have been made to introduce this system into England they have been condemned by the general sense of the Royal and the Chemical Society.

THE MANGANESE WATERS OF EXCELSIOR SPRINGS.

By W. P. MASON.

A CONSIDERABLE amount of a manganese salt in spring water is so unusual an occurrence that the following analysis may prove of interest:—

Excelsior Springs is a small town about thirty miles north-east of Kansas City, Mo., and has grown up on account of the increasing fame of its chalybeate waters, the curative powers of which are recognised throughout a large section of the western country.

Manganese is reported (usually as carbonate) in some sixty-two springs in the United States, but in nearly half of these it exists in traces only, and in the great bulk of the remainder the amount present is but small. In seven instances the manganese equals or exceeds the amount present in the Excelsior water, but in all but two of these seven (and these doubtful) the element is present as sulphate or chloride, while the Excelsior water contains it as carbonate only. Occurring, as it does, associated with ferrous carbonate, it readily places the water in a favourable light to medical practitioners for use in anæmia and kindred troubles, inasmuch as combinations of manganese and iron are so much more effective than the iron preparations alone. The fact of the manganese being in the readily-assimilated carbonate form, gives advantage over the more astringent sulphate and chloride.

MnCO ₃		9.41	parts per million.
Al ₂ O ₃		2.10	" "
SiO ₂		12.00	" "
K ₂ SO ₄		4.86	" "
NaCl		17.60	" "
FeCO ₃		23.43	" "
CaCO ₃		362.75	" "
MgCO ₃		54.70	" "
KCl		2.80	" "
NaHCO ₃		9.35	" "
		492.00	" "

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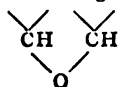
THE CONSTITUTION OF CELLULOSE.

By C. F. CROSS and E. J. BEVAN.

IN recent communications (CHEMICAL NEWS, ix., 163, and *Your Chem. Soc.*, lvii., 1) we have recorded certain observations on the ethereal derivatives of cellulose—acetates and benzoates—the study of which was undertaken with the view to throw light on the constitutional problem, which for this, as for perhaps the greater number of the carbohydrates, remains unsolved. In preparing the benzoates we start from the hydrates precipitated from the solution of cellulose (cotton) in ZnCl₂.Aq, which we find to be soluble, under certain conditions, in solutions of the alkaline hydrates. The general behaviour of these hydrates is suggestive of the forms of cellulose found in the growing parts of plants. Certain of these we have found to yield furfural on hydrolysis (H₂SO₄.Aq), and we therefore, assuming a similar behaviour in this respect also, investigated the conditions under which the typical cellulose could be made to yield this aldehyd in such quantity as to establish between them an essential relationship. On heating purified cotton with zinc chloride solution (50 per cent) and raising the temperature gradually to 120—135°, furfural is formed, and distills with the water in such quantity that a drop of the distillate strikes a deep crimson with aniline acetate.

While we are pursuing the investigation so as to determine the quantity formed, and the maximum yield under the most favourable conditions, it may not be out of place to call attention to the bearing of the result upon the problem in question. Assuming a unit group of C₆, which appears to be justified by Franchimont's researches, the presence in this of three alcoholic OH groups is established by the formation of a triacetate and trinitrate, under what we may regard as normal conditions of such transformations. In acetylising cellulose in presence of zinc chloride, an acetate is obtained which, from our

analyses and determinations of yield, appeared to be a pentacetate. The formation of such a derivative indicates either the existence of additional OH groups, or the hydrolysis of aldehydic groups, condensed to build up the complex anhydride which cellulose probably is, with conversion of the resulting pairs of OH-groups into the corresponding OAc. In the absence of direct evidence of the presence of aldehydic or ketone oxygen we have inclined to the former view (*Fourm. Chem. Soc.*, lvii., 4), but it would now appear, from the formation of furfural under the conditions above named, that the latter is the more probable explanation, indicating, as it does, the existence of aldehydic oxygen in the cellulose molecule. And further, the remaining O atom of the C₆ unit would also be accounted for as existing in a—



group. To such a view the lines of evidence appear to us to be converging, and at least there is sufficient ground for adopting it as a working hypothesis. On this view the higher acetate is derived, not from the original cellulose, but from a hydrate of lower molecular weight.

In studying the condensation of the carbohydrates, Tollens usually employs sulphuric acid. Our experiments tend to show that zinc chloride is to be preferred, as oxidation is excluded, and the action can be pushed to a higher temperature without complicating the results. We find also that the ligno-celluloses readily yield to this reagent, giving derivatives (hydrates) soluble in alkaline solutions, to some extent also in water, i.e., on diluting the solution in ZnCl₂Aq and filtering off the precipitated hydrate, the solutions contain dissolved carbohydrates, which, on concentrating, are resolved with formation of furfural. It is probable that the ligno-celluloses could be made to yield a much larger proportion of wood-gum (holzgummi) and xylose by previous treatment with this reagent than by direct treatment with the ordinary hydrolytic reagents.

In the light of these results the so-called wood-gum is seen to be more closely related to the typical cellulose than has been supposed.

ON OPENING UP PYRITES IN A CURRENT OF OXYGEN.

By P. JANNASCH.

THE author communicates a simplification of the process for opening up pyrites in the dry way, resulting from experiments on its behaviour with oxygen at a red heat. If pulverised pyrites are heated in a glass tube in a current of oxygen, there soon sets in vivid incandescence, accompanied with a shower of sparks, and extends quickly through the entire mass. There appears an odour of sulphurous acid, there follow vapours of sulphur trioxide, and drops of sulphuric acid condense on the cold parts of the tube; if the heat is applied too suddenly sulphur sublimes. The decomposition is perfect, since the residue of dark red ferric oxide dissolves, excepting the small quantities of quartz and gangue present. This fact rendered it possible to improve the author's proposed method for opening up pyrites in a current of air and nitric acid. He uses in the ignition of pyrites the apparatus described in his former paper, with the modification that the air-holder is filled with oxygen and the bottle with nitric acid is omitted. The flexible caoutchouc tube connecting the drying-cylinder with the combustion-tube can be closed by a pinch-cock.

Above all things, the heating of the porcelain boat containing the substance has to be very carefully regulated at the commencement. The author begins with the hindmost flame, which must not be more than an inch in

height, and waits until the boat begins to glow before extending the ignition as the reaction proceeds. With care any spirting of the substance or sublimation of sulphur can easily be avoided. The current of oxygen must not be too rapid, about 200 bubbles per minute. If too large a quantity of sulphuric acid vapour appears in the first receiver, the current of oxygen must be arrested momentarily by closing the pinch-cock. After a full half-hour has expired, the tube is strongly ignited for about a quarter of an hour in order to ensure the decomposition of all the material and to expel all the sulphuric acid; the tube is then allowed to cool a little in the current of oxygen, the boat is drawn out of the tube (which is still hot), and the current of oxygen is broken off. The sulphurous acid formed is substantially oxidised to sulphuric acid by the bromine in the first two receivers. The liquid in the receivers is poured into a beaker, mixed with a few c.c. of strong hydrochloric acid, the bulk of the bromine present is removed by evaporation, and the sulphuric acid is precipitated with barium chloride. By this method it is possible to determine the sulphur in pyrites with the needful accuracy in the space of four to six hours.—*Journal für Praktische Chemie*.

SEPARATION OF ZINC FROM NICKEL.

By H. ALT and J. SCHULZE.

IN a solution of zinc and nickel containing a sufficiency of succinic acid, a current of sulphuretted hydrogen precipitates all the zinc as a perfectly white zinc sulphide, whilst the nickel remains in solution. The liquid may be either hot or cold, and an excess of the precipitant is not objectionable. The succinic solution must be free from salts, as otherwise nickel sulphide may be simultaneously precipitated.

The authors give an especial description of the analysis of nickel silver. The alloy is dissolved in nitric acid, which is almost entirely driven off by heat, the stannic acid is filtered off, and the copper is precipitated with sulphuretted hydrogen. The filtrate is evaporated down to a small volume, the sulphuretted hydrogen being expelled. Potassa-lye is then added almost to neutrality, and the liquid is precipitated with 10 to 20 drops of a 10 per cent solution of sodium acetate. The precipitate of basic iron acetate is filtered off, any excess of acetic acid is expelled by boiling the filtrate with an addition of a mineral acid, and the bases are precipitated with sodium carbonate at a boiling heat. The zinc and nickel carbonates are filtered off, washed, and dissolved in succinic acid, filtered if needful, the liquid made up to a known volume, and an aliquot part of the liquid is taken for further treatment. The authors take from 1.5 to 2 grms. of the alloy, make up the solution to 500 c.c., and take 100 c.c. for further treatment. There are added 5 grms. succinic acid, the liquid is slightly diluted with water, heated almost to a boil, and treated with a current of sulphuretted hydrogen until it smells strongly of the gas. It is then let stand for twenty-four hours, filtered, the white zinc sulphide is washed, and determined as such.

The filtrate is mixed with a little hydrochloric acid (to prevent any deposition of nickel sulphide on heating in consequence of the great dilution of the succinic acid), and the hydrosulphuric acid is expelled by evaporation. The liquid is then treated at a boiling heat with potassa-lye, when nickelous oxide is precipitated quantitatively even in presence of much succinic acid.—*Berichte der D. Chem. Gesellschaft und Chemiker Zeitung*.

Molecular Weights of Metals.—W. Ramsay.—The author gives the molecular weight of lithium as 7.03 by experiment and 7.02 by calculation; that of sodium, 12.1 and 11.52; cadmium, 102.9, 112.0; thallium, 181.0 and 204.0, &c.—*Ztschr. f. Physik. Chem.*, Vol. iii., Part 4.

THE TREATISE OF DEMOCRITUS ON THINGS NATURAL AND MYSTICAL.

Translated by ROBERT R. STEELE, F.C.S., &c.

(Concluded from p. 114).

GLOSSARY AND REMARKS.

(The references are to Pliny's "Natural History.")

- Alum.** (35, 15). Was generally an astringent salt of Fe or Al. Alum from Melos was a true alum and is still obtained there.
- Androdamas.** (36, 20; 37, 54). Arsenical pyrites; from its silvery lustre used with silver.
- Antimony.** (33, 33, 34). Is invariably the sulphide. The metal was obtained by the ancients, but confused with lead.
- Aphroselinum.** Selenite, sulphate of lime, &c.
- Aristolochia.** (25, 8). Birth-wort.
- Arsenic.** (34, 28). Orpiment, As_2S_3 .
- Asterites.** Identical with androdamas.
- Auriconchylum.** Gold in powder, coquille d'or.
- Bronze** is here used for a metal of which copper is the principal constituent.
- Cadmia.** (34, 1). Generally calamine; sometimes the "furnace calamine," ZnO , containing Cu, Pb, Sb, and As. (A passage in Strabo, liii., p. 419, Ed. 1587, fo., shows metallic zinc to have been worked in his time, and called false silver).
- Ceruse.** (34, 18). White-lead.
- Chalcant.** (34, 12). Copperas, $FeSO_4$, of course containing copper. From the vitreous crystals are derived the words "vitriol," &c.
- Chalcites.** (34, 12). Copper pyrites, $CuFeS_2$.
- Chian Earth.** (35, 16). A white substance like fuller's earth.
- Chrysiis.** (33, 6; 35). A mixture of silver and lead, which becomes yellow on heating. Davy thought it massicot, yellow oxide of lead.
- Chrysocolia.** (33, 5). Malachite; or a solder for gold, 9, 29. The name means "gold glue." It did not contain borax.
- Cimolia.** (35, 17). Cimolite, a fuller's earth.
- Cinnabar.** (33, 17). Minium, Pb_3O_4 , was sometimes spoken of under this name.
- Claudianum** was a metal, named from its manufacturer. An alloy of Sn and Pb, with Cu, Zn, &c.
- Cnicus.** (21, 15). Carthamus tinctoria, the safflower; still used as a tinctorial agent.
- Cobastia.** Arsenical fumes of furnaces (in which cobalt was first found).
- Cyanus.** (37, 9). Blue carbonate of copper, Azurite.
- Electrum.** (23, 4). An alloy of gold with more than 20 per cent silver, amber coloured.
- Ecumenicus flower.** Herb basil?
- Flower of Copper.** (34, 11). Small black scales of oxide of copper, which separate on cooling.
- Fove.** Tin.
- Luna.** Silver.
- Magnesia.** (36, 16). Any white body, steatite; as in XVI., an amalgam; an ore of iron. Workmen in mines now are accustomed to call any white ore unknown to them magnesia.
- Misy.** (34, 12). Roman vitriol, a mixture of $CuSO_4$ with basic sulphate of iron; oxidised copper pyrites.
- Molybdochalium.** An alloy of Cu and Pb.
- Nitre.** (31, 10). A white salt. Pliny's description answers to sal ammoniac, may be Na_2CO_3 , KNO_3 , Na_2SO_4 , &c., &c.
- Orichalium.** (33). Yellow copper ore, mountain brass; or white copper, an alloy of Cu and As.
- Oxymel.** (23, 2). Vinegar and honey.
- Persea.** (13, 9). Balanites Æg. Berthelot translates it peach.
- Lead.** (34, 16). *White*, is Sn; *Black*, is Pb.

Pyrites. (36, 19). *White*, arsenical pyrites. *Yellow*, iron pyrites.

Sal Cappadocia. A variety of sal gemma.

Sandarach. (34, 18). As_2S_2 (realgar) or HgS .

Scissile. Alum schist; any ore distinguished by a laminated structure, saline efflorescence, and styptic properties; yellow ochre colour.

Sol. Gold.

Sory. (34, 12). Basic sulphate of iron, brown from exposure, containing $CuSO_4$.

Silver Spume. (33, 6). Argentiferous litharge.

Venus. Copper.

The gold and silver varnishes still used to brighten the colour of gold and silver alloys are nearly identical with those given in this work.

THE IGNITING-POINT OF SULPHUR.

By J. RUTHERFORD HILL.

THIS note is the result of some experiments suggested by a letter in the CHEM. NEWS (vol. lxi., p. 95). Mr. Bertram Blount there states that in the course of a recent conversation a remark was made to the effect that sulphur ignites at a temperature not far above its melting-point ($107^\circ C.$). On referring to published authorities, Mr. Blount was apparently puzzled by the very discordant statements on the subject, which ranged from $115^\circ C.$ to $293^\circ C.$ He makes an appeal to any one who has determined the igniting-point of sulphur to publish the result and indicate the method employed. What follows is intended as a reply to his appeal.

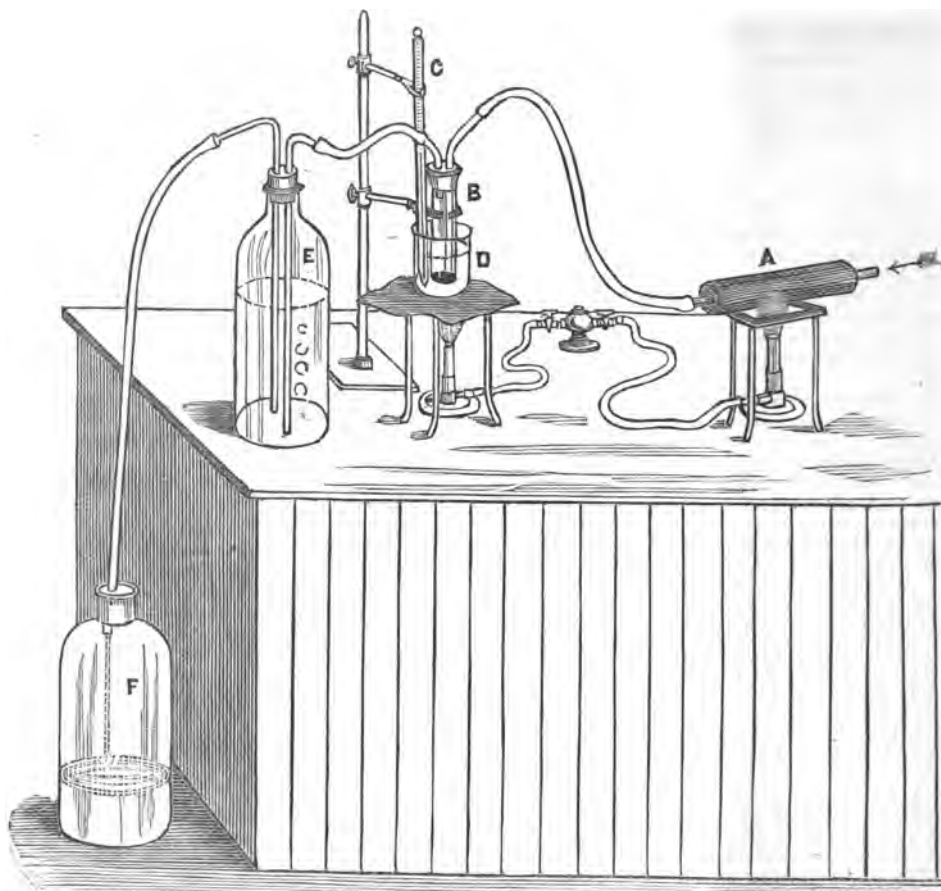
It will be convenient to state here the published igniting-points of sulphur quoted by Mr. Blount as follows:—Tidy, $115^\circ C.$ to $120^\circ C.$; Dumas, $150^\circ C.$; Pelouze et Fremy, $150^\circ C.$; Miller, $235^\circ C.$ to $260^\circ C.$; Watts, $250^\circ C.$; Dalton, $260^\circ C.$; Thomson, $293^\circ C.$

After some little planning and experiment the following method was adopted as being the least open to objection:—A test tube, B, size $5 \times \frac{1}{2}$ inches, is fitted accurately with a cork perforated for two glass tubes. The inlet tube, A, passes to about 1 inch from the bottom of the test-tube, so as to carry the air down to the surface of the sulphur. The outlet tube, A', stops at the entrance to the test-tube; the outlet tube is connected with the aspirator, E, which is emptied by a syphon tube into the receiver, F, and thus draws a current of fresh air through the whole apparatus in the direction indicated by the arrow.

To prevent cooling of the test-tube the fresh air is heated by covering a portion of A with wire gauze and keeping it nearly red hot by a Bunsen flame. By this means it was found that when the current was passing freely the air entered the test-tube at a temperature of about $60^\circ C.$, and when made to pass slowly the temperature was considerably higher.

A portion of the sulphur to be tested was placed in the test-tube, B. The test-tube is immersed, along with a thermometer, C, in a bath of strong sulphuric acid boiling at $332^\circ C.$ contained in the beaker, D, which is heated by a Bunsen flame. When the thermometer indicates a temperature of about $120^\circ C.$, the test-tube, B, is lowered into the bath, and the air current started by lowering the receiver, F, beneath the level of the aspirator, E.

As the temperature rises, vapour of sulphur, mixed with air, fills the test-tube and passes over into the aspirator. There would be risk that when the flashing-point is reached the mass of vapour in the aspirator might also be fired and cause damage. This risk is avoided by causing the outlet tube, A', to pass down to the bottom of the column of water in E and below the level of the syphon tube. By this means direct communication between the vapour in B and that in E is cut off.



When the thermometer reached 255°C. , the vapour of sulphur burst into flame; this occurred several times on repeating the experiment; on one occasion it inflamed at 253°C. , and once or twice at slightly higher temperatures. On pinching the india-rubber syphon tube with the hand, the air current is stopped, the test-tube fills with sulphur vapour, and the flame is instantly extinguished. On removing the pressure from the syphon tube, fresh air immediately enters the test-tube and the sulphur vapour instantly rekindles. This takes place with great sharpness, and the operation can be repeated with great ease and rapidity. By removing the Bunsen flame from the bath, *v.*, the temperature rapidly falls, and the sulphur flame can be extinguished and re-kindled at every degree. This continues till the thermometer falls to 248°C. , but below that temperature the vapour will not re-ignite. The experiment was repeated eight or nine times with the same result. On one occasion the thermometer was read 246°C. when the flash last appeared, but this was possibly a mistake in observation.

An experiment was now made to ascertain if the sulphur inside the tube was at the same temperature as that indicated by the thermometer in the sulphuric acid bath outside. A thermometer was placed in a test-tube containing sulphur. This test-tube was placed in the sulphuric acid bath. On applying heat it was found that while the temperature was rising, the sulphur inside the test-tube was always at few degrees lower temperature than the sulphuric acid outside. On withdrawing the heat and allowing the temperature to fall, however, it was found that both thermometers speedily indicated the same temperature, and continued to fall at the same rate.

This would indicate that the point at which the sulphur flame was first seen (255°C.) was probably not the real temperature inside the tube, and also that the point at which the flame ceased while the thermometer was falling (248°C.) was the real temperature inside the tube. To test this point the sulphuric acid bath was raised once to 261°C. and at another time to 271°C. , and on both occasions the flame disappeared on allowing the temperature to fall to 248°C.

Mr. D. B. Dott has kindly tested my thermometer by a comparison with a standard instrument, and the foregoing temperatures have been corrected accordingly.

From these results it would appear that the igniting-point of sulphur in air is 248°C. , and that the temperature stated by Watts (250°C.) is most nearly correct. It may be noted that the sulphur used was sublimed sulphur of ascertained purity and free from moisture.

Pharmaceutical Society of Great Britain,
36, York Place, Edinburgh.
February 19, 1890.

On the Dioxyposphinic and Oxyphosphinous Acids.—J. Ville.—The aldehyds unite with hypophosphorous acid to form two new classes of acids:—(1) Trivalent and monobasic acids, the dioxyposphinic acids, formed by the direct union of the elements of 2 mols. of aldehyd and 1 mol. of hypophosphorous acid; (2) divalent and monobasic acids, resulting from the direct combination of hypophosphorous acid and aldehyd, mol. to mol.—*Comptes Rendus*, Vol. cx., No. 7.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLETT, F.R.S.,
Professor of Chemistry in the University of Virginia.

(Continued from p. 116).

A PRELIMINARY course of experiments was carried out with plates of pure electrolytic copper (both pairs) in solutions of cupric sulphate, in order to test the effects, if any, of the following differences in the conditions of the two electrolysis cells compared.

1. *Effect of Difference in the Degree of Concentration of the two Solutions.*—The solution in one of the two vessels in which the plates were immersed being made to contain but one-tenth the proportion of cupric sulphate existing in the other, acidification and all other conditions being the same for both, only a very minute difference was found between the quantities of copper deposited in the same time on the two cathode plates, and the difference was not invariably in the same direction. The tendency, however, seemed on the whole to be toward a slightly larger amount thrown down from the stronger than from the weaker solution. In every case there was decidedly more copper dissolved from the anode than was deposited on the cathode plate.

2. *Effect of Difference in Acidity of two Solutions, otherwise of the same Strength.*—With the same proportion of cupric sulphate in both solutions, one was made to contain but one-tenth as much free sulphuric acid as the other; all other conditions remained the same for both. As before, the difference of result was insignificant, and somewhat variable in direction, with an apparent tendency towards a very slightly greater deposit on the cathode plate in the less acid as compared with the more acid solution. As before, there was in every case a distinctly greater loss of copper from the anode than gain on the cathode plate, especially in the more acid solution.

3. *Effect of Difference in Temperature of the two Solutions.*—The proportion of cupric sulphate and of free acid being the same for both solutions, and all other conditions the same, one of the two, however, being maintained at 72°, 47°, or 37° C., while the other was at 2° C., thus establishing a difference in temperature of 70°, 45°, or 35° respectively, there was distinctly in every instance rather more copper thrown down on the cathode plate in the colder than in the warmer solution. The loss of weight of the anode plate was always greater than the gain at the cathode, and the difference in this respect was greater in the warmer than in the colder solution.

4. *Effect of Difference in the Size of the Plates.*—All other conditions being the same in both the electrolysis cells, the plates in one were made to present but one-fourth the surface of those in the other, so that the "current density" was proportionally increased in the former. Under these circumstances there was a constant, though but small difference in the amount of copper deposited on the two cathodes, the quantity being greater on the cathode plate with the smaller surface. The tendency seemed to be towards a greater excess of metal removed from the anode over that deposited on the cathode plate in the case of the larger plates, as compared with the smaller.

5. *Effect of Difference in the Distance between the Plates.*—The plates of both pairs being equal in size, and all other conditions being uniform, the plates in one of the two electrolysis cells were placed at a distance apart only one-fifth that intervening between those of the other pair. It was not clear that any constant difference of result could be detected, but the tendency seemed to be rather toward a very slightly greater deposit on the cathode plate in the case in which the plates were farther apart as compared with that in which they were nearer

together. There was no recognisable difference in the proportion of metal dissolved off from the anode plate.

Similar experiments were made with two pairs of plates of pure silver, thus checking the results obtained with copper, and contrasting the behaviour of one at least of the less chemically alterable metals with that of the more easily alterable copper. It was intended to make a set of similar experiments also with gold plates only, but the available supply of pure gold in the form of rolled plates was not sufficient for the numerous experiments required. The silver solution used was one of potassium argento-cyanide, and the substitute for the free sulphuric acid of the copper experiments was an excess of potassium cyanide. The results obtained were essentially similar to those of the copper experiments, the effect of difference in temperature between the two solutions being, however, less decided, and the slight effect of difference in the size of the plates ("density of current") less constant and distinct.

In all the preceding experiments it was found that the most constant results under otherwise similar conditions were obtained by using feeble currents rather than those of greater strength, especially in the case of the silver solutions. There seemed, however, to be a limit to this. On the whole, the most satisfactory results were obtained (both in these preliminary experiments, and in those aiming at the atomic weight determination) with currents not exceeding $\frac{1}{10}$ th of an ampère per square c.m. of surface of (one side of) the opposed plates, and in some cases a current but one-fifth of this maximum was used.

Having in view the indications afforded by the preliminary experiments, it was determined to use tolerably strong solutions of the metals to be deposited with not more than a moderate excess of free acid, or, in the case of the double cyanide solutions, excess of potassium cyanide, to maintain the same temperature in both the electrolysis cells, and to have their temperature as low as possible (about 2° C.), and to have the plates of the two metals to be compared equal in size, and at equal distances apart, using a weak electric current, and keeping watch over its strength by means of an ordinary hydrogen voltmeter in the circuit.

In the actual experiments on the deposition of gold as compared with silver it was originally proposed to use a solution of potassium auri-cyanide against one of potassium argento-cyanide, with the expectation that 3 atoms of silver would be thrown down for 1 atom of gold. But the first attempts made showed clearly that this reaction could not be obtained. The comparison as to gain in weight of the gold and silver cathode plates gave results leading to an atomic weight for gold impossibly high if the silver deposited were taken to represent 3 atoms, and much too low if it were taken to represent but 1 atom. Hence it appeared that the potassium auri-cyanide had been partially, but not completely, reduced to auro-cyanide by the action of the current, and an intermediate result obtained as to the equivalent quantity of silver between that due to the one or the other gold salt if exclusively present.

A change was therefore made to the auro-cyanide in the preparation of the solution to be electrolysed. A pure form of potassium cyanide was prepared with the aid of alcohol, and carefully tested as to the absence of any metal capable of deposition from the watery solution on electrolysis. Auric chloride was precipitated by ammonia the fulminating gold, after washing, dissolved in a strong solution of this potassium cyanide by the aid of heat, and the auro-cyanide crystallised out by cooling. The crystals were washed, re-dissolved in water, auro-cyanide separated from the solution by evaporation with hydrochloric acid, and the crystalline powder after cautious washing again dissolved in potassium cyanide solution, using for the purpose the barely necessary amount of the solvent liquid, but afterwards adding a further quantity, so as to have potassium cyanide in excess. Potassium argento-cyanide was prepared by precipitation of a solu-

* A Paper read before the Royal Society, May 9, 1889.

tion of pure silver in nitric acid with the purified potassium cyanide, washing the precipitate, and re-solution with the aid of the necessary quantity of potassium cyanide, of which finally a moderate excess was added.

The solutions of the gold and silver salts were made of equivalent strength, for the most part at the rate of 7 grms. of metallic gold for each 100 c.c. of solution, and an approximately corresponding amount of silver, taken atom for atom. Both solutions received the same excess of potassium cyanide, generally equal to one-half of that already present in the double salt, but in some of the experiments it was found necessary to add yet more during the electrolysis in order to preserve the purely metallic character of the surface of the plates. As an additional security against the admixture of auri-cyanide with the auro-cyanide of the gold solution, it was subjected for some time to electrolysis with unweighed gold plates immersed, these being reversed two or three times in position, just before the introduction of the weighed plates for a quantitative experiment. A number of attempts were made to substitute for the solution of potassium auro-cyanide one of sodium auro-thiosulphate, of potassium or sodium auri-chloride, and of simple auric chloride, in the last two cases employing at the same time a solution of silver nitrate, but these efforts led to no success.

In many of the experiments made with the double cyanide solutions the cathode plates, both of gold and silver, after removal from the electrolysis cells and thorough washing, were found to curl up on being heated, the deposit, which in these cases was rather hard and brittle, swelling up in a remarkable way, with formation and bursting of little blebs, or minute bubbles of the metallic surface, and parting off to some extent of the deposit from the original plate underneath. When the heating was carried out in the Sprengel vacuum small but quite appreciable amounts of hydrogen were found to be given off, having been occluded in the metal deposited. It seemed necessary to throw aside the results in all cases in which this condition of the deposit was well marked. Other experiments were vitiated by the gold deposit not being thoroughly compact, and still others by the surface not being clearly metallic, aurous cyanide making its appearance from the solution. It was hoped that in the experiments, free from apparent defect, any irregular behaviour of the gold solution at first might be got rid of by continued electrolysis, with reversal of the anode and cathode plates when necessary, until the ratio of gold to silver deposited should become constant; but confidence in this was greatly shaken when an instance occurred, followed afterwards by others, of sudden change in this ratio, attended with much less loss from the anode gold plate than the gain of the opposed cathode plate, pointing to the deposition of gold from the auro-cyanide with simultaneous formation of auri-cyanide in the solution.*

Altogether but five experiments were made in this way, yielding results which seemed worthy of being used to determine the atomic weight of gold, and it is of course unsatisfactory to know that these were selected out of a much larger number, mainly because, while not known to be in any way vitiated by apparent defects, they lead to values for the atomic weight in question close to those obtained by other methods and other experimenters. It is possible that this near approach to agreement may merely result from a balance of errors in opposite directions, which taken separately would have caused the experiments to be rejected. Some other experiments, under apparently similar conditions, gave figures for the atomic

weight differing from those reported by one or two whole units.

These only admissible results are the following:—

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited. Grms.	Silver deposited. Grms.
I.	A, b	B	5.2721	2.8849
II.	"	"	6.3088	3.4487
III.	"	"	4.2770	2.3393
IV.	"	"	3.5123	1.9223
V.	"	"	3.6804	2.0132

Aside from other difficulties liable to be encountered in carrying out this electrolytic method, the two most important sources of possible inherent error which suggest themselves are the occlusion of hydrogen by the metallic deposit and the instability of the atomicity of gold in the solution electrolysed.

The separation of hydrogen on the cathode plate, whether in bubbles (which may be avoided by proper regulation of the current) or occluded by the metal (which does not seem to be completely avoidable with any current, although the amount of occluded gas was extremely small in a number of my experiments), must be ascribed to decomposition, simultaneous with that of the cyanide of gold, either of water or, more probably, of cyanide of potassium, with secondary action of the potassium on the water. In either case, it is by no means clear that the proportion of current giving rise to this liberation of hydrogen can be counted upon as the same in the gold solution and in that of silver; and hence, even though it be fairly assumed that Faraday's principle of equivalent electrolysis by the same current is strictly correct for the *ensemble* of chemical actions in the two cells, the portion of current actually concerned in depositing gold or silver only in each of the respective cells may conceivably not be quite the same, so that the weights of the two metals thrown down may not be strictly equivalent.* It was, therefore, deemed important to work with feeble currents, and, while heating all the plates in a Sprengel vacuum before weighing, to reject the results of all those experiments in which the quantity of gas thus discharged amounted to more than the merest trace. But, if the source of error in question still exist at all, it might affect the atomic weight of gold in comparison with that of silver, either by making the former appear higher or lower than the truth.

The source of error most to be feared, however, in connection with the application of this electrolytic method to the determination of the atomic weight of gold, is the uncertainty of having all the gold throughout the process in the form of potassium auro-cyanide in the solution, in view of the transition observed to auri-cyanide during electrolysis, although change in the opposite direction occurs with even greater ease. Each of the two salts appears to admit of electrolytic decomposition, and the presence of any traces of the auri-cyanide, in which the gold has triad character, while the calculation is based on the supposed presence of monad gold only would, of course, tend to make the atomic weight of the metal appear lower than the truth.

(To be continued).

* As bearing on the question of the simultaneous decomposition of two electrolytes in the same solution, the following results may be recorded of an experiment made with a solution of mixed zinc and copper sulphates, with excess of potassium cyanide, the anode plate being of brass and the cathode plate of platinum, and an analysis made of the proportions of the two metals in the anode plate, in the solution as first taken, and in the alloy deposited on the cathode plate and subsequently dissolved off from it by means of nitric acid

Proportion of copper to zinc.	In the brass anode plate.	In the solution electrolysed.	In the alloy deposited on the cathode plate
Copper	68.74	13.81	73.34
Zinc	31.26	86.19	26.66
	100.00	100.00	100.00

Different results would undoubtedly have been obtained by substituting some other metal for one of those taken.

* Hittorf (Poggendorff, *Annalen*, [4], vol. xvi., p. 523), in the simultaneous electrolysis of gold and silver solutions, the gold as potassium auri-chloride, obtained results which showed that this metal was deposited at the rate of 1 atom for 3 of silver. Calculating on this basis from his two experiments, the atomic weight of gold comes out = 196.311 and 194.197; for silver 107.66.

In one experiment of my own, using sodium auri-chloride, the result showed that the gold was thrown down for the most part as a triad, but partly as a monad, element.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 6th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Joseph Barker, 8, St. James's Street, S.W.; Charles Ridgeway Beck, 181, High Street, Burton-on-Trent; David Corrie, Nobel's Explosives Company, Polmont Station, N.B.; Andrew Cowan Holborn, B.Sc., 10, West Garden Street, Glasgow; Herman Lescher, 61, Egerton Gardens, South Kensington; Henry de Mosenal, 220, Winchester House, Old Broad Street, E.C.; James S. H. Walker, 304, Morningside Road, Edinburgh.

The following were elected Fellows of the Society:—Frederick Alfred Anderson, B.Sc., Percival Babington, G. Russell Beardmore, M.D., Richard Berncastel, Bertram Blount, Robert Frederick Blake, Henry Herbert Bunting, William Burton, Paul Alexander Cobbold, John Dennant, Frank Gossling, John Charles Jackson, John S. Lumsden, Alfred E. Macintyre, Frederick Mills, Ira Moore, John Myles, Robert Richard Rothwell, Edward Sergeant, M.D., Basil William Valentin.

The President announced that the senior Secretary would attend the meeting to be held in Berlin on March the 11th, to celebrate the 25th anniversary of Professor Kekulé's benzene theory, and would present the following address from the Society.

"The President and Council of the Chemical Society, on behalf of British Chemists, desire to offer to Professor August Kekulé their warmest congratulations on the occasion of the Twenty-fifth Anniversary of the promulgation of his theory of the Constitution of Aromatic Compounds.

The influence which the felicitous conception of Benzene as a closed chain has had on the development of chemical theory, the impetus which it has imparted to the study of the intricate problems of isomerism among the derivatives of this and similar compounds, and the guidance which it has afforded in an industry of such magnitude and importance as that of the Coal Tar Colours, is universally recognised; and it is with special pleasure that the countrymen of Faraday, the discoverer of Benzene, recount these benefits while paying honour to their author.

This theory found the chemistry of even the immediate derivatives of benzene an almost untilled field; it has transformed it into a fertile province, to which have been annexed regions the very existence of which was unknown.

May it long be permitted to you, Professor Kekulé, whose work has been so full of suggestion and inspiration, to remain witness to the benefits which continue to flow from your fruitful generalisation."

The following papers were read.

16. "Some Crystalline Substances obtained from the Fruits of various Species of Citrus." By WILLIAM A. TILDEN, D.Sc., F.R.S., and CHARLES R. BECK.

The authors have examined the solid matters which are deposited from freshly extracted oils of limes, lemons, and bergamot made by hand. The substance from oil of limes (*C. limetta*), after purification by repeated crystallisations from alcohol containing a little potash, forms small pale yellow needles, united in tufts, which melt at 121–122°. It is proposed to name this substance *limettin*. It is not an acid nor a glucoside. It is not acted on by acetyl-chloride nor by phenylhydrazine. Analysis leads to the formula $C_{16}H_{14}O_6$. When submitted to the action of bromine it affords a tribromo-derivative, $C_{16}H_{11}Br_3O_6$, which crystallises in colourless

scales. When boiled with a concentrated solution of soda limettin loses an acetyl-group, yielding a substance very similar to itself in appearance and properties, $C_{14}H_{11}(OH)O_4$. When fused with potash it yields phloroglucol and acetic and formic acids.

Essence of lemon yields a substance similar to limettin in appearance, though the crystals are more lustrous and melt at 116°. Concordant analyses led to the formula $C_{14}H_{14}O_6$, which contains 2C less than the formula of limettin.

Bergamot yields a crystalline compound differing from both the preceding. It forms colourless distinct prisms melting at 270–271°. The examination of this substance will be continued when a supply of material has been obtained.

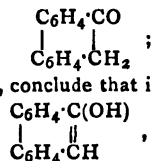
These substances are entirely distinct from the compounds which, under the name of auranitin, hesperidin, limonin, have been obtained by other chemists from various fruits of the orange and lemon tribe.

The two former of these are glucosides. Hesperidin has been shown to be a derivative of phloroglucol, and in its origin is probably connected with the substance described under the name limettin in this paper.

17. "Reduction of α -Diketones." By FRANCIS R. JAPP, F.R.S., and FELIX KLINGEMANN, Ph.D.

Benzil was boiled for a few minutes with fuming iodhydric acid, and after removal of the iodine the product was distilled under reduced pressure: an excellent yield of *deoxybenzoin* was obtained.

Phenanthraquinone, subjected to the same treatment, yielded the so-called *phenanthrone*, which Lachowicz, who prepared this compound by the reduction of dichlorophenanthrone (from phenanthraquinone and phosphorus pentachloride), regarded as the deoxybenzoin of phenanthraquinone,—



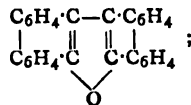
the authors, however, conclude that it is a phenol, viz.,—

as it is not acted on by phenylhydrazine, and when heated with acetic anhydride forms an acetyl-derivative (m. p. 76–77°). When Lustgarten's test for β -naphthol (shaking the solution in caustic potash with chloroform) is applied to it, like β -naphthol, it affords a strong Prussian blue colouration, the colouring matter separating in blue needles with a coppery lustre. This interaction is to be further studied.

By boiling phenanthraquinone with acetic acid, to which a small quantity of strong iodhydric acid together with some amorphous phosphorus had been added, *monacetylphenanthraquinol*,—

$C_{14}H_8(OH)(OC_2H_5O)$, was obtained, identical with the compound prepared by Klinger (*Annalen*, ccxlix., 138) by the direct interaction of aldehyd and phenanthraquinone in sunlight.

By distilling acetylphenanthraquinol under reduced pressure, two compounds were obtained: a substance which distilled over, and which crystallised from benzene in red plates, melting at 155°, giving on analysis, C, 84.0, H, 4.7 per cent; and a second substance, which sublimed into the neck of the flask, condensing in the form of needles, melting at 295–297°, and giving figures agreeing with the formula $C_{28}H_{16}O$. The authors obtained a compound which they believe to be identical with this by heating acetylphenanthraquinol with concentrated chlorhydric acid at 200–210°; it is possibly *tetraphenylene-furfuran*,—



the last-mentioned mode of formation being analogous to that in which lepidin (tetraphenylfurfuran) is obtained from benzoïn.

18. "Studies on Isomeric Change, No. IV. Halogen-Derivatives of Quinone (First Notice)." By ARTHUR R. LING.

The experiments of Hantzsch and of Nietzki have proved in opposition to those of Levy, that the "anilic" acids are paradihydroxy-derivatives, and Hantzsch and Schnitter have shown that an isomeric change occurs when paradichloroquinone is brominated, the product being metadichlorometadibromoquinone. The author has made several attempts to prepare the paradichlorodibromoquinone, but hitherto unsuccessfully; in so doing he has obtained results which confirm Hantzsch and Schnitter's conclusion.

Metadichlorodibromoquinone is formed on brominating paradichloroquinone or diacetylparadichloroquinone in acetic acid solution, also by the chlorination of paradibromoquinone, the isomeric change apparently occurring in the first and last mentioned cases at the ordinary temperature. By brominating diacetylparadichloroquinol dissolved in carbon tetrachloride in the presence of a trace of iodine, a diacetyldichlorobromoquinol has been obtained, which melts at 260—270°; this may, however, be a mixture of isomerides.

Metadichlorobromoquinone is obtained by brominating metadichloroquinone, and also together with the paradichloro-derivative by brominating paradichloroquinone. It forms yellow plates which do not show a sharp melting point (175—180°); it is sparingly soluble in cold alcohol, easily in boiling. On treatment with potash it yields chlorobromanilic acid. The quinol formed by reducing it with sulphurous acid separates from chloroform in white needles melting at 135°, sparingly soluble in cold water or in chloroform but easily in the boiling liquids. On acetylation it yields a diacetyl-derivative which crystallises from alcohol in white needles melting at 174—180°.

Paradichlorobromoquinone is formed, together with its isomeride, on brominating paradichloroquinone. It is somewhat more soluble in the ordinary solvents than its isomeride, and melts at 158—159°. On treatment with potash it yields chloranilic acid.

Paradichlorobromoquinol crystallises from water in long transparent monohydrated needles which melt at 124—126°; they easily lose their water, becoming opaque, and then melt at 132—135°. Re-crystallised from chloroform, the substance melts at 135.5°: it possesses about the same solubility in all the solvents tried as its isomeride. Hence the two cannot be separated by crystallisation. On acetylation it yields an acetyl-derivative, which crystallises in silky needles melting at 148—159°, sparingly soluble in cold dilute alcohol, but easily in boiling.

When paradichlorobromoquinone is brominated at the ordinary temperature, a product is obtained which may perhaps contain paradichlorodibromoquinone, since, on treatment with potash, it affords a mixture of chlorobromanilic and bromanilic acid. In this way the author hopes to succeed in isolating paradichlorodibromoquinone.

19. "Note on a Phenyl Salt of Phenylthiocarbamic Acid." By AUGUSTUS E. DIXON, M.D.

When heated together in equimolecular proportions at 140—150°, phenol and phenylthiocarbamide interact, forming phenylic phenylthiocarbamide, $\text{NHPh}\cdot\text{CSOPh}$, but the yield is very small; this salt forms octahedral crystals resembling sulphur in appearance, melting at 150°.

20. "Contributions to the Chemistry of Thiocarbamides. Interaction of Benzyl Chloride and of Allyl Bromide with Thiocarbamide, Phenyl- and Diphenylthiocarbamides." By EMIL A. WERNER.

An account is given of the first part of an investigation of the action of benzyl chloride and allyl bromide on thiocarbamide and its different phenylated homologues. After reviewing the results already obtained by Claus,

Bernthsen and Klinger, and Will and Rathke in the same direction, the following compounds are described:—

$\text{C}_8\text{H}_{10}\text{N}_2\text{S}\cdot\text{HCl}$, m. p. 174°, and the base $\text{C}_8\text{H}_{10}\text{N}_2\text{S}$, m. p. 88°, from benzyl chloride and thiocarbamide.
 $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}\cdot\text{HCl}$, m. p. 112°, and the base $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$, m. p. 81—82°, from benzyl chloride and phenylthiocarbamide.

$\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}\cdot\text{HCl}$, m. p. 152—153°, and the base—
 $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}$,

a viscid liquid, from benzyl chloride and diphenylthiocarbamide.

$\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{HBr}$, m. p. 84°, from allyl bromide and thiocarbamide; the base could not be isolated in a pure state.

$\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}\cdot\text{HBr}$, a viscid liquid, from allyl bromide and phenylthiocarbamide; the base forms a syrupy fluid which is very unstable.

$\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}\cdot\text{HBr}$, m. p. 170—171°, and the base—
 $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}$,

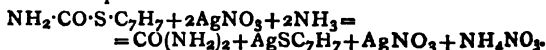
m. p. 57°, from allyl bromide and diphenyl thiocarbamide.

The decomposition of the bases by dilute sulphuric acid at 170° (Will's reaction) is studied, and it is shown that the primary thiocarbamide-derivatives behave in a different manner to the homologues.

Characteristic mercurio-chlorides possessing somewhat similar properties have been obtained from the several compounds: the compound $\text{C}_8\text{H}_{10}\text{N}_2\text{S}\cdot\text{HCl}\cdot\text{HgCl}_2$ may be taken as an example; it melts at 112°, and at 136° decomposes with loss of a molecular proportion of HCl and simultaneous alteration in the position of the alkyl-group (benzyl).

The sulphates and picrates of the bases are described, and in the case of the compound $\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{HBr}$, from $\text{C}_3\text{H}_5\text{Br}$ and CSN_2H_4 , a chromium alum has been obtained, $(\text{C}_4\text{H}_8\text{N}_2\text{S})_2\text{Cr}_2(\text{SO}_4)_4\cdot 24\text{H}_2\text{O}$.

Benzyl thiocarbamate ($\text{CONH}_2\cdot\text{SC}_7\text{H}_7$) and benzyl phenylthiocarbamate ($\text{CONHC}_6\text{H}_5\cdot\text{SC}_7\text{H}_7$) were incidentally prepared: both compounds combine with two molecular proportions of AgNO_3 ; the resulting products are immediately decomposed by ammonia in accordance with the equation—



At the Meeting on March 20 Professor Judd, F.R.S., will deliver a lecture on "The Evidence afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressures."

PHYSICAL SOCIETY.

March 7, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

SIR H. MANCE and Messrs. L. R. Shorter, C. Thompson, and A. D. Waller were elected Members.

Dr. S. P. THOMPSON described "*Bertrand's Refractometer*," and exhibited the capabilities of the instrument before the Society.

Its action depends on total reflection. The refractometer consists of an hemisphere of glass about 8 m.m. diameter set at the end of a tube, the plane face being outwards and inclined at about 30° with the axis. One side of the convex surface of the hemisphere is illuminated through a piece of ground glass set about perpendicular to the plane face. The hemisphere is viewed through an eyepiece focussed on a scale divided to tenths of millimetres, placed within the tube. The instrument is particularly useful for mineralogical specimens and liquids. The procedure in the latter case is to smear a film of the liquid over the plane face of the hemisphere, and, by

looking through the eyepiece, determine the scale reading of the line which separates the light and darker portions of the field. A reference to a calibration table gives the refractive index.

In experimenting with solids, a thin film of very dense liquid (supplied with the instrument) is placed between the specimen and the glass, and the procedure is then as above. The refractive index of opaque solids can be determined in this way. In using the instrument for minerals, great care must be taken not to scratch the glass. The handiness of the refractometer and its perfect portability (its dimensions being about 5 c.m. long by 2½ c.m. diameter) are great recommendations.

Mr. BLAKESLEY asked to what accuracy the scale could be read, and whether the sensitiveness of the instrument was at all comparable with that of other methods.

Prof. DUNSTAN enquired if it could be used with volatile liquids.

In reply, Dr. THOMPSON said that with non-homogeneous light the scale could be read to one division, but, with a sodium flame, one-tenth of a division could be estimated. For volatile liquids a drop may be used instead of a film, or the evaporation of a thick film may be retarded by a cover-glass.

Mr. H. TOMLINSON's paper on "The Villari Critical-Point in Nickel" was postponed.

Prof. DUNSTAN described an "Apparatus for Distilling Mercury in a Vacuum," devised by himself and W. Dymond, and showed the working of the arrangement.

It consists of a 3 m.m. soft glass tube, rather more than a metre long, having an oblate spheroidal bulb blown at the upper end. The bulb is placed over a ring burner. At the top of the bulb a tube of 1.5 m.m. diam. is attached, and this passes outside the bulb, and descends close to the larger tube. The part of the smaller or fall tube just below the bulb is enlarged, so as to form a condensation chamber, and the lower part serves as a Sprengel tube. A conical reservoir, containing the mercury to be distilled, is in flexible connection with the lower end of the large tube, as in Clark's well-known apparatus. The advantages claimed for the new apparatus are its relative shortness and portability, the small quantity remaining undistilled, and its non-liability to derangement if left unsupplied with mercury.

To ensure satisfactory working, a constant pressure of gas is necessary, and this is obtained by inserting a Sugg's dry governor in the supply pipe. During distillation, peculiar green flashes are seen within the condensation chamber, and these are intensified by bringing it near an electric machine in action. The apparatus also serves well to show the character of an electric discharge through mercury vapour, for the mercury in the two tubes may be used as electrodes.

Prof. THOMPSON said he devised a simple form of distilling apparatus some time ago, which answered fairly well, and could be made by any amateur glass-worker. It consisted of a double barometer, one leg of which was of small bore, so as to act as a Sprengel tube. The rising part of the bend at the top of the larger tube was expanded, and served as the evaporating chamber, below which a burner was placed.

The PRESIDENT asked why Clark's apparatus is made so lengthy.

In reply to this question Mr. BOYS said that, as the fall tube goes down within the rising one, the mercury near the top of the latter is heated by the condensing mercury (thus economising gas), and hence condensation does not take place until the vapour has passed a considerable distance down the fall tube.

Prof. S. U. PICKERING read a paper on "The Theory of Osmotic Pressure, and its Bearing on the Nature of Solution."

The author said that considerable doubt exists as to the accuracy of the premises on which the theory is

based, and if the theory is to be regarded as true, and not merely a rough working hypothesis, the following conditions must be fulfilled by weak solutions:—

(1). The molecular depression of the freezing-point must be independent of the nature of the dissolved substance.

(2). Any deviations from (1) must be in the direction indicated by the theory.

(3). The depression must be independent of the nature of solvent.

(4). The depression must be independent of the amount of solvent (all solutions being weak).

(5). The deviations with strong solutions should be in the theoretical direction, and

(6). They should be regular.

Prof. PICKERING proceeded to show that experiment, instead of confirming the above statements, disproves them all.

As regards (1), without counting abnormally low (half) values, Raoult's results show variations of 60, 40, 30, &c., per cent in different cases, and the author quoted other values where the variations were 500, 260, 230, &c., per cent. These variations he considered were too great to be explained by the fact of the solutions used being three or four times too strong.

Referring to (2), he said that low values are reasonably explained by the polymerisation of the dissolved molecules, high values by their dissociation into ions. He then argued that there are no abnormally high values, for the view that such exist and that they are explainable by dissociation involves the following conclusions:—(a) That the more stable a substance is, the more easily it is dissociated; (b) that solution dissociates molecules which we know can exist undissociated as gases; (c) that water must consist of 1½H₂O, and the atomic theory is wrong; (d) that energy can be created, and therefore the theory of its conservation is untenable.

With respect to (3) it was pointed out that in many instances the same dissolved substance gives the full depression with one solvent and half depression with another. Cases were quoted where the depression produced by the same dissolved body in different solvents showed variations of 36,000, 21,000, and 28,000 per cent.

In discussing (4) the author said that even with solutions weaker than that corresponding to a gas, the law is not fulfilled. Taking the case of sulphuric acid (the only one at present fully investigated), the variations amount to 40 per cent, or about 28 times the experimental error.

With reference to (5) it was stated that with strong solutions the molecular depression should become smaller, but in every known case (nine were quoted) it becomes larger, the increase in one instance being 3200 per cent.

As regards (6) all experimental data available, especially those relating to sulphuric acid, show that the deviations are neither regular nor always in the same direction.

Mr. T. H. BLAKESLEY said he was greatly interested with Prof. Pickering's paper, for some time ago he was induced to make experiments on the volume of salts in solution by reading Joule's papers on that subject. Some of the results confirmed, but others did not agree with Joule's theory, that the molecular volume in solution was a whole number. If this theory was true then, he said, it would be possible to pre-determine the density of solutions, and from the measured density of any known solution we could determine the water of crystallisation of the salt from the formula—

$$n = \frac{1 - \frac{W}{w}(D - 1)}{D} \left(\frac{A}{H_2O} + x \right)$$

where W and w are the masses of the water and salt respectively, D the density of the solution relative to water at the same temperature, A the molecular weight of the dehydrated portion of the salt, x the number of molecules of water, and n the molecular volume of the salt in solution, the two latter being whole numbers.

CORRESPONDENCE.

PRIESTLEY AND LAVOISIER.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (vol. lxi., p. 84) I notice an interesting letter from H. C. B., giving some French versions—or perversions?—of the persecutions of Joseph Priestley. It is curious that the authors did not feel themselves on perilous ground, since, if England mobbed and drove out Priestley, France guillotined Lavoisier outright! Strictly speaking, neither Priestley nor Lavoisier can rank as a "martyr of science." If the former had followed the wise counsel of Edward Gibbon, and "stuck to physics and chemistry," not a dog would have barked at him. And Lavoisier suffered, not as a *savant*, but as a "*fermier général*."—I am, &c.,

J. W. SLATER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 7, February 17, 1890.

Electrolysis by the Igneous Fusion of Aluminium Oxide and Fluoride.—Adolphe Minet.—The author seeks to utilise this kind of electrolysis as the point of departure of a series of applications of electricity to chemistry with especial reference to the production of metallic aluminium. His best results have been obtained with an iron cathode, the intensity of the current being 975 ampères and the difference of potential at the electrodes 6·1 volts. Under these circumstances the weight of aluminium deposited was 1900 grms., as against a calculated quantity of 2320 grms., or a yield of 82 per cent.

On Sodium Silicoglucinate.—P. Hautefeuille and A. Perrey.—The authors caused neutral sodium vanadate to act upon mixtures of silica, glucina, and alkali. The sodium silico-glucinate differ in composition and form from the corresponding potassium compounds.

Part Played by Foreign Bodies in Irons and Steels; Relation between their Atomic Volumes and the Allotropic Transformations of Iron.—F. Osmond.—Prof. W. C. Roberts-Austen, in his researches on the effect produced on the mechanical properties of gold by the addition of 0·20 per cent of one of seventeen foreign metals, had pointed out a curious relation between the results obtained and the position of the alloying metals in the periodic classification, and had suggested that an analogous relation should occur in iron. M. Osmond has elaborated this idea, and finds that foreign bodies of low atomic volume tend to cause iron to assume or to retain that one of its molecular forms in which it possesses the least atomic volume; substances of high atomic volume produce an inverse effect. Carbon, whilst obeying the general law, undergoes, at a certain critical temperature, a transformation, the nature of which is still doubtful, though its existence is incontestable.

On Dibromo-Carballylic Acid.—E. Guinochet.—Not adapted for useful abstraction.

Determination of Uric Acid in Urine by Means of a Solution of Sodium Hypobromite, with the Aid of Heat.—M. Bayrac.—The author evaporates 50 c.c. of urine in the water-bath; in the residue he precipitates the uric acid by 5 or 10 c.c. of a solution of hydrochloric acid at $\frac{1}{2}$ and washes with alco-

hol. This treatment removes urea and creatinine and leaves pure uric acid. This latter body is dissolved in the water-bath with 20 drops of soap-boiler's soda (l) and treated at 90°—100° with 15 c.c. of a concentrated solution of sodium hypobromite. The nitrogen is given off quantitatively from a hot solution.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., January, 1890.

Study of Various Questions of General Chemistry. Lecture by Prof. Schützenberger, of the College of France.—This paper is too long for insertion.

Gallisine, a Non-Fermentible Ingredient of Commercial Glucose.—Dr. Schmidt.—It is found that the glucose obtained by the action of non-arsenical sulphuric acid upon starchy matters is not pure, but contains a substance incapable of fermentation, gallisine. It is obtained as a very fine white powder, perfectly amorphous and very hygroscopic. It is insoluble in anhydrous ether, chloroform, and the hydrocarbons, except absolute alcohol (which dissolves it with difficulty), methylic alcohol, and glacial acetic acid. Its aqueous solution has a distinctly acid reaction. It is not precipitated by lead acetate and basic acetate, by mercury chloride and acetate, iron chloride, tincture of iodine, barium and calcium chloride. Its composition is represented by the formula $C_{12}H_{24}O_{10}$. The author has examined a number of derivatives, especially barium gallisate, hexacetyl-gallisine, potassium and lead gallisates. He has further studied the behaviour of gallisine with chlorosulphonic acid and with bromine and when heated in a current of hydrogen: the products of the dry distillation of gallisine with lime, its oxidation by nitric acid, its transformation under the influence of the pancreatic secretion, its conversion into glucose; its behaviour with the liquors of Fehling and of Knapp, and its optical properties. It is dextro-rotatory, the deflection ranging from 25·6° to 84·40°, according to the strength of the solution. In the analysis of eleven samples of commercial starch-sugar the quantities of gallisine found were from 22·49 to 6·82 per cent.

The Molecular Weights of the Metals.—From the *Journal of the Chemical Society*.

Determination of the Specific Gravity of Salts Soluble in Water.—J. W. Retgers.—From the *Zeitschrift für Physikalische Chemie*.

Absorption of Carbonic Acid by Mixtures of Alcohol and Water.—O. Müller.—The coefficient of absorption decreases as the proportion of alcohol in the mixture augments and reaches its minimum, when the mixture contains 28 of alcohol. It then increases until it reaches the coefficient of absorption of pure alcohol.

Determination of the Molecular Weights of Substances in Solution.—HH. Will and Bradig.—From the *Berichte D. Chem. Gesell.*

Decolourising Effects observed during the Electrolysis of Acidulated Water.—H. N. Warren.—From the CHEMICAL NEWS.

Some Phosphates of Polyvalent Metals.—K. R. Johnson.—The author has examined the composition, crystalline form, specific gravity, and molecular volume of lanthanum and cerium metaphosphate, uranium phosphate, iron (ferric) chrome, aluminium and thorium metaphosphate, and yttrium pyrophosphate.—*Berichte*.

Solubility of Glass in Water.—HH. Mylius and Foerster.—Water does not dissolve glass, but decomposes it into silica and free alkali. Glass containing lead is least attacked by boiling water.

On Melezitose.—M. Alechine.—The author concludes that melezitose has the molecular composition $C_{18}H_{32}O_{16}$. These two papers are from the *Journal Rousskago Physico-chimicheskago Obozretstva*.

Synthesis of Glycerins by the Aid of Hypochlorous Acid.—Sergius Reformatsky.—This paper does not admit of useful abstraction.

Combinations of Raffinose with Bases.—MM. Beythien and Tollens (*Berichte*).—Raffinose forms with bases compounds some of which are less soluble in water and alcohol than raffinose.

Xylose and Wood-Gum.—MM. Wheeler and Tollens (*Berichte*).—Xylose, like arabinose, gives the well-known cherry-red colour when heated with phloroglucinol and hydrochloric acid.

Action of Chloral upon Glucose.—A. Heffter (*Berichte*).—A mixture of glucose and chloral heated to 100° for one to two hours is resolved into two compounds, $C_6H_{11}O_6Cl_3$.

Constitution of Primuline.—HH. Pfützinger and Gattermann.—Not adapted for useful abstraction.

Electrolytic Separation of Cadmium and Zinc.—Edgar E. Smith and Lee K. Frankel.—From the *American Chemical Journal*.

Presence of Tin in Certain Sugars.—Dr. T. L. Phipson.—From the *CHEMICAL NEWS*.

Determination of Sulphuric Acid in Presence of Iron.—HH. Jannasch and T. W. Richards.—From the *CHEMICAL NEWS*.

Determination of Silica and Iron in Cryolite.—R. Fresenius and E. Hintz.—Already inserted.

Condensation of Hydrochloric Acid.—Dr. Hurter.—From the *Journal of the Society of Chemical Industry*.

The Chilian Manganese Ore.—J. Pattinson and H. S. Pattinson.—From the *Journal of the Society of Chemical Industry*.

On the So-called Resin Colours.—A. Muller-Jacobs (*Dingler's Polyt. Journal*).—The precipitates obtained by treating the aqueous solution of a resin soap are treated with a metallic salt. They combine with all the basic aniline colours, forming compounds known as resin-colours.

The Density Numbers of the Elements.—J. A. Groshans.—Already noticed.

Metallurgical Review.—An account of nickel steel, of the tenacity and ductility of aluminium bronzes and brasses, an examination of boiler-plates while working, and a notice of ferro-silicon alloyed with white cast-iron.

A Lake of Borax in California.—Napier Hake.—From the *Journal of the Society of Chemical Industry*.

Preparation of Artificial Meersehaum.—A. von Loseke.—From the *Zeitschrift für Angewandte Chemie*.

Crossing Varieties of Cinchona.—From the *Pharm. Journal*.

Canagire.—Henri Tremble.—This product, now coming into use in tanning in America, is the root of *Rumex hymenosepalum*. Sturk found in this root 28.57 per cent of tannin, but the author finds only 17.33.

New Application of Potassium Ferricyanide.—G. Kassner (*Chemiker Zeitung*).—A mixture of hydrogen peroxide, and a solution of potassium ferricyanide rendered alkaline by potassa, soda, or caustic baryta, may be used for giving off a rapid and regular current of pure oxygen.

Industrial Review and Various Patents.—Brief notices of patents relating chiefly to artificial colours.

Royal Institution of Great Britain.—The following are the probable arrangements for the Friday Evening Meetings after Easter:—

Sir Frederick Bramwell, Bart., D.C.L., F.R.S., on "Welding by Electricity"; on Friday, April 18th.

Sir John Lubbock, Bart., M.P., D.C.L., LL.D., F.R.S., on "The Shapes of Leaves and Cotyledons"; on Friday, April 25th.

Walter H. Pollock, M.A., on "Théophile Gautier"; on Friday, May 2nd.

R. Brudenell Carter, F.R.C.S., on "Colour-Vision and Colour-Blindness"; on Friday, May 9th.

Professor Raphael Meldola, F.R.S., on "The Photographic Image"; on Friday, May 16th.

Professor A. C. Haddon, M.A., M.R.I.A., Dean of Royal College of Science, Dublin, on "Manners and Customs of the Torres Straits Islanders"; on Friday, May 23rd.

A. A. Common, F.R.S., Treas. R.A.S., on "Astronomical Telescopes"; on Friday, May 30th.

Professor W. Boyd Dawkins, M.A., F.R.S., on "The Search for Coal in the South of England"; on Friday, June 6th.

Absorption of Gases in Liquid Mixtures.—O. Müller and O. Lubarsch (*Annalen der Physik und Chemie*).—The absorption-coefficient of carbon dioxide, hydrogen, oxygen, and carbon monoxide in mixtures of alcohol and water falls as the concentration of the alcohol increases, reaches a minimum of 28 per cent (by weight), and then increases.

Determination of Mercury.—J. Volhard.—In a solution containing the mercury as a mercuric salt the acid is almost entirely neutralised with pure sodium carbonate, and the mercury is completely precipitated with ammonium sulphide, avoiding too great excess. It is advantageous to use ammonium sulphide recently prepared with the strongest ammonia. Soda-lye is then added with agitation until the liquid begins to clear; it is then heated to boiling, adding more lye until the sulphide is entirely dissolved and the liquid is quite clear. The caustic soda used should be that prepared from the metal, ascertaining previously the absence of silver. From the alkaline solution the sulphide is precipitated at a boiling heat by ammonium nitrate, keeping up the boiling until the ammonia is nearly expelled, and the precipitate is let settle in heat. It is denser, and deposits more rapidly than the precipitate obtained with sulphuretted hydrogen. If the precipitate has to be brought upon a tared filter, it is best first to wash by decantation with boiling water until the washings no longer react with a solution of silver nitrate. If, after the precipitation of the sulphide, it has been boiled so long that it may be possibly contaminated with sulphur, a little sodium sulphite is added and it is again boiled for a short time.—*Liebig's Annalen*.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Hydropyridines.—Will any reader kindly inform me where I can obtain a full account of the hydropyridine series of organic compounds?—INTERESTED.

Schäfer's Beta-naphthol Beta-sulphonic Acid.—I should feel grateful for any information respecting the mode of preparation of the above, or reference to any works dealing with the subject.—"Q."

Are Cast-iron Stoves Prejudicial?—I have heard it stated (1) that carbon contained in the cast-iron is driven off, when the stove is sufficiently heated, in the form of carbonic oxide; (2) that the iron, thus becoming more porous, absorbs carbonic oxide (CO) from the fire itself, and again poisons the air of one's room with it. As I have lately taken into use a cast-iron stove (slow combustion—burning coke—sides lined with firebrick), and infer that a quantity of CO is formed in it, from the blue flames which ignite as soon as the feed door at the top is opened, I should be greatly obliged for any information on either of the above points.—C. E. H.

MISCELLANEOUS.

Chemical Society Anniversary Meeting.—The Anniversary Meeting will be held at 4 p.m. on Thursday, March 27th. Fellows and their friends will dine together at the Whitehall Rooms, Hôtel Métropole, at 7 p.m. the same evening.

MEETINGS FOR THE WEEK.

- MONDAY, 17th.**—Medical, 8.30.
Society of Arts, 8. "Some Considerations Concerning Colour and Colouring," by Prof. A. H. Church, M.A., F.R.S.
- TUESDAY, 18th.**—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
Society of Arts, 5. "Brazil," by James Wells, M.Inst.C.E.
Institute of Civil Engineers, 8.
Pathological, 8.30.
- WEDNESDAY, 19th.**—Society of Arts, 8. "Commercial Geography," by J. S. Keltie
Meteorological, 7.
- THURSDAY, 20th.**—Royal, 4.30.
Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
Royal Society Club, 6.30.
Institute of Electrical Engineers, 8.
Chemical, 8. "The Evidence Afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressures," by Prof. Judd, F.R.S.
- FRIDAY, 21st.**—Royal Institution, 9. "Electro-magnetic Radiation," by Prof. G. F. Fitzgerald, M.A., F.R.S.
Physical, 5. "On the Villari Critical-point of Nickel," by Herbert Tomlinson, F.R.S. "On Bertrand's Idiocyclophanous Prism," by Prof. Sylvanus Thompson.
- SATURDAY, 22nd.**—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

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BOROUGH OF DARLINGTON.

SPENT OXIDE.

The Gas Works Committee invite offers for the Purchase of about 100 Tons (more or less) of SPENT OXIDE.

Samples and Particulars may be had on application to the Gas Works Engineer, Town Hall.

Tenders, endorsed "Tender for Spent Oxide," to be sent to me not later than the 20th instant.

No pledge is given that the highest or any offer will be accepted.

(By Order)

F. T. STEAVENSON.

Darlington, 7th March, 1890.

Town Clerk.

BOROUGH OF DARLINGTON.

The Gas Works Committee invite Tenders for the Supply of 100 Tons of PEROXIDE OF IRON for Gas Purification, delivered at the Darlington North Road Station; delivery to extend over a period of not exceeding six months from the acceptance of the Tender.

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No pledge is given that the lowest or any Tender will be accepted.

(By Order)

F. T. STEAVENSON,

Darlington, 7th March, 1890.

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This Exhibition will be held at the Crystal

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Prospectuses and Application forms for space may be had from the Hon. Secretary (Geo. A. Ferguson, Editor of the *Mining Journal*) at the Offices, 18, Finch Lane, E.C.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1582.

THE NITRIFYING PROCESS AND ITS SPECIFIC FERMENT.*

By PERCY F. FRANKLAND, Ph.D., B.Sc. (Lond.),
A.R.S.M., &c.
Professor of Chemistry in University College, Dundee,
and GRACE C. FRANKLAND.

The process of nitrification has been practically studied for centuries, but it was first in the year 1878 that it was shown by Schloessing and Müntz to be dependent upon the presence of certain minute forms of life, or micro-organisms, or, in other words, to be a fermentation change.

The authors have been engaged during the last three years in endeavouring to isolate the nitrifying organism, and the present memoir gives in detail an account of the numerous experiments which were made in this direction.

Nitrification, having been in the first instance induced in a particular ammoniacal solution by means of a small quantity of garden soil, was carried on through twenty-four generations, a minute quantity on the point of a sterilised needle being introduced from one nitrifying solution to the other. From several of these generations gelatin-plates were poured, and the resulting colonies inoculated into identical ammoniacal solutions, to see if nitrification would ensue; but, although these experiments were repeated many times, on no occasion were they successful.

It appeared, therefore, that the nitrifying organism either refused to grow in gelatin, or that the authors had failed to find it, or that, growing in gelatin, it refused to nitrify after being passed through this medium.

Experiments were, therefore, commenced to endeavour to isolate the organism by the dilution method. For this purpose a number of series of dilutions were made by the addition, to sterilised distilled water, of a very small quantity of an ammoniacal solution which had nitrified. It was hoped that the attenuation would be so perfect that ultimately the nitrifying organism alone would be introduced.

After a very large number of experiments had been made in this direction the authors at length succeeded in obtaining an attenuation consisting of about 1-1,000,000th of the original nitrifying solution employed, which not only nitrified, but, on inoculation into gelatin-peptone, refused to grow, and was seen, under the microscope, to consist of numerous characteristic bacilli hardly longer than broad, which may be described as bacillo-cocci.

These results are the more striking, for, in the case of the two other bottles similarly diluted, one had not nitrified, but, on inoculation into gelatin-peptone, produced a growth already on the second day, whilst the remaining bottle not only produced a growth, but had also nitrified, thus clearly showing that the number of organisms had been reduced to two, i.e., one which nitrified and did not grow in gelatin, and another which did nothing to do with nitrification, but which grew in gelatin. In the case where nitrification took place and a growth also appeared in the gelatin-tube, it was obvious that both the nitrifying and non-nitrifying organisms were present. These inoculation tests, together with the microscopical appearances, were confirmed by repeated experiments, with invariably the same results.

It is, however, very remarkable that, although this bacillo-coccus obstinately refuses to grow in gelatin when inoculated from these dilute media, yet in broth it pro-

duces a very characteristic growth, which, although slow in commencing, often requiring three weeks before it makes its appearance, is very luxuriant.

The authors have, moreover, been successful in inducing nitrification in ammoniacal solutions inoculated from such broth cultivations, the extent of which has been quantitatively determined.

Although microscopically its form differs slightly when grown in broth and the ammoniacal solution respectively, yet its identity was established beyond question by its returning to its characteristic bacillo-coccus form when grown again in the ammoniacal solution.

The authors have also been able to induce its tardy growth in gelatin-peptone by passing it first through broth cultivations.

The paper is accompanied by carefully executed drawings of the nitrifying organism when grown in the various media employed.

NOTE ON THE ISOLATION OF THE NITRIFYING ORGANISM.

By R. WARINGTON, F.R.S.

ON March 13, Prof. P. F. Frankland and Mrs. Frankland communicated to the Royal Society an account of their investigation on the isolation of the nitrifying organism. As I have myself been working for some time on the same subject, I desire to make a few remarks on their communication.

The medium they made use of was an ammoniacal solution containing no organic matter; this was originally seeded with a small quantity of garden soil. From this solution, when nitrified, a second solution was seeded, from the second a third, and so on, through 24 cultures.

From these nitrified solutions gelatin plates were prepared. The organisms which appeared upon the gelatin were introduced into ammoniacal solutions perfectly similar to those from which they had been originally obtained, but in no case did any nitrification take place.

The authors next resorted to the dilution method, and after many trials succeeded, by seeding from a nitrified solution diluted to one million times its volume, in obtaining nitrification in an ammoniacal solution, which, when nitrified, yielded no growth on gelatin. This nitrifying organism they describe as a small bacillo-coccus; one of its special characteristics, as already mentioned, is that it will not grow on gelatin.

My own work, which is as yet unpublished, has been conducted on similar lines; and, as far as it has gone, entirely confirms the statements made in the earlier part of Frankland's communication.

Having prepared successive cultures of the nitrifying organism in weak solutions of ammonium carbonate, containing the necessary nutritive salts, but no organic matter, I proceeded to isolate the bacteria present by means of plate cultures, or by Klein's method of spreading with a loop of platinum wire an extremely thin film of the solution, diluted if necessary, over a sloping surface of nutrient gelatin contained in a test-tube. The growths on gelatin were in all cases simple in character, and from three solutions only one organism was obtained. As these solutions had actively nitrified, and were fully capable of setting up nitrification in other solutions to which they were added, the probability seemed strong that the single organism obtained from them was in fact the nitrifying agent. This organism, however, and also all the other organisms previously separated by culture on gelatin from nitrifying solutions, obstinately refused to nitrify when introduced either alone or in mixture into fluids susceptible of nitrification. In a written Report made to the Managing Committee of the Rothamsted Agricultural Trust on Feb. 14, I gave an outline of these results, and said "We must therefore assume either—

* Abstract of a Paper read before the Royal Society, March 13, 1890.

(1) That the nitrifying organism does not grow on gelatin, or (2) that it loses its property of nitrification when so grown." The experiments I had then in hand were specially designed to test the truth of the second alternative.

I have employed the dilution method to a limited extent. Seeding with a nitrified solution diluted to 500 times its volume, I failed in two instances to obtain nitrification, while in three instances nitrification took place; in all the latter cases I obtained the usual growth on gelatin.

The nitrifying organism described by Frankland appears to agree in form with the small oval coccus originally mentioned by Schloesing and Müntz, but the isolation and characters of which were so imperfectly described that it was difficult to know what amount of weight should be given to their statement.

It is important to note that the bacterium isolated by Frankland produces only nitrous acid. This is quite in accordance with my own long experience of what occurs when successive cultures are made from a nitrifying fluid; the product soon becomes purely nitrous, and the nitrites thus produced are quite permanent. We must therefore suppose either that the production of nitric acid requires the presence of two organisms, one of which disappears during successive cultures; or else that the nitrifying bacterium suffers a diminution of power during artificial cultivation. That the formation of nitric from nitrous acid may be brought about by a second organism I am in a position to assert, but this of course does not exclude the possibility of the second alternative.

I hope, before long, to communicate to the Chemical Society the full results of my investigation.

ON THE PERIODIC LAW.

By JOHN A. R. NEWLANDS, F.I.C., F.C.S.

In the *Chemical Society's Journal* for October last (No. 323, p. 638), in the Faraday Lecture, by Prof. Mendeleeff, on the Periodic Law of the Chemical Elements, an erroneous statement occurs which is doubtless due to an accidental oversight on the part of the distinguished lecturer. He refers to a Table of mine published in the *CHEMICAL NEWS* (vol. xii., p. 83), and gives its first and last horizontal lines in the following way:—

1st Octave of
Newlands H F Cl Co and Ni Br Pd I Pt and Ir
7th ditto... O S Fe Se Rh and Ru Te Au Os or Th

Now the complete table from which the above lines were taken was as follows:—

No.	No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 26	Pd 36	I 42	Pt & Ir 50	
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 53	
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Cd 38	Ba & V 45	Pb 54	
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56	
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52	
N 6	P 13	Mn 20	As 27	Di & Mo 34	Sb 41	Nb 48	Bi 55	
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51	

NOTE.—Where two elements happen to have the same equivalent, both are designated by the same number.

This Table contained the whole of the then known elements, numbered off in the order of their atomic weights and arranged with a few slight transpositions so as to bring members of the same group on the same horizontal line.

A similar Table was shown at the Meeting of the Chemical Society, March 1, 1866, except that the last vertical column of elements in it was given absolutely in numerical order, thus:—

	No.
Pt and Ir	50
Os	51
Hg	52
Tl.. ..	53
Pb	54
Bi	55
Th	56

It will be seen that in Prof. Mendeleeff's illustration of my table, the ordinal numbers have been entirely omitted. In addition, the symbols on his upper line are described as my "1st octave," and those on the lower line as my "7th octave," whereas on my system, which follows the natural order of the atomic weights, the 1st octave comprises the eight elements from H to F, as shown in the above table.

I have long since pointed out that when the elements are arranged in the natural order of their atomic weights "the difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note of an octave in music" (*CHEM. NEWS*, vol. x., p. 94, Aug. 20, 1864). Now there could be no eighth note in the octave unless there were seven consecutive notes preceding. In fact, an octave in music has been defined as "a collection of eight consecutive notes." Taking the natural notes on the key-board of a piano for instance, commencing with the first note, say A, it, and all consecutive notes up to and including the next A, would be termed the first octave, but it would be incorrect and quite inadmissible to describe all the A's on the key-board as belonging to the first octave, or all the G's as belonging to the seventh octave.

Laboratory, 27, Mincing Lane, E.C.,
March 18, 1890.

A NEW METHOD FOR THE ANALYSIS OF ZINC AND COPPER ALLOYS.

By H. N. WARREN, Research Analyst.

THE following method of separation of zinc from copper and other allied metals, which was introduced by the author at the commencement of the present year, and is now being satisfactorily worked in several commercial laboratories, depends chiefly upon the superior affinity of magnesium to replace not only copper and metals of the same group, but, by suitable means, to effect a complete separation of such oxidisable metals as zinc, iron, &c. The method, although speedy and accurate, is perhaps

better suited in cases where an approximate idea is known as to the nature of the alloy qualitatively. In the case of the sample presented being a brass alloy, which should, for convenience sake, be obtained in the form of filings, a suitable weighed quantity is introduced into a small conical flask, to which is added strong H_2SO_4 in proportion to the quantity of sample taken. On applying a gentle heat from a sand-bath for a few minutes the alloy is quickly rendered soluble, and the whole diluted with

water to a convenient bulk. A few coils of magnesium tape are now introduced into the solution and the solution maintained at about 100° F., until the whole of the copper is precipitated, which is ascertained by the absence of a red precipitate upon the addition of a drop of potassium sulphocyanide to the filtrate. The precipitated copper, which should be of a perfect red colour, is filtered, and finally washed into a tared platinum dish by the aid of a small quantity of ether, and dried in the air-bath, from whence the weight is readily obtained by the usual method. If tin, antimony, or other metals of the same group are suspected, the copper must necessarily be further examined.

To the filtrate is added a somewhat strong solution of sodium acetate, and the whole raised to the boiling-point; by this means any free sulphuric acid is neutralised, all the iron that may be present is precipitated as tribasic acetate, and the sulphate of zinc present converted into acetate. Into this is introduced a further quantity of magnesium, and, in this instance, the form of thick sheet or rod is better adapted than that of tape, the precipitated zinc being the more readily detached from the same. Upon the introduction of the magnesium a brisk reaction follows, accompanied by a copious supply of hydrogen, the zinc being entirely precipitated, inasmuch that not the slightest precipitate is obtained on the addition of ammonia and ammonium sulphide to the filtrate, the zinc thus obtained being treated as in the former instance, which, if successfully performed, shows very slight signs of oxidising.

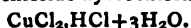
Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

THE VOLUMETRIC DETERMINATION OF COPPER.

By A. ETARD and P. LEBEAU.

We cannot estimate copper accurately by any rapid method, for the electrolytic method, which is perfect, requires some time. Various volumetric processes have been proposed, but in none of them is the end of the operation shown with certainty.

One of the most expeditious methods is that in which the yellow colour of a copper salt dissolved in an excess of strong hydrochloric acid is made to disappear by means of a stannous solution. The colouration observed is due to a cupric chloride hydrochlorate,—



The yellow colour not being very intense, it is not easy to note the end of the determination.

Recently there has been pointed out a colour reaction of copper produced in presence of sulphuric acid and potassium bromide. The reaction, however, is due to the cupric bromide in presence of strong hydrobromic acid, without the participation of sulphuric acid. There is probably formed a violet hydrobromate of cupric bromide.

The colouration is developed in mediums containing only CuBr_2 , HBr , and H_2O as necessary elements. A small excess of water turns the violet colour to an ordinary copper green.

The authors use this bromo-cupric colouration as an indicator for the volumetric determination of copper.

Any salt of copper whatever, in a strong solution, treated with an excess of concentrated hydrobromic acid, takes a violet colour like that of permanganate. Such a solution, if mixed with a standard solution of stannous bromide or chloride dissolved in strong hydrobromic acid, scarcely grows paler, and at the end it is abruptly decolorised by a single drop of the stannous liquid. The time during which the stannous liquid is run in must not be too prolonged, as on contact with air the violet colour is reproduced.

The process is relatively costly, but we may use, with-

out inconvenience, a solution of stannous chloride in strong hydrochloric acid, free from iron.

The stannous solution is, in any case, run into the concentrated solution of the cupric salt after the addition of a few c.c. of strong hydrobromic acid. The portion taken for analysis must be free from oxidising and reducing agents.

The standard of the stannous solution must be verified from time to time.—*Comptes Rendus*, vol. cx., p. 408.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLETT, F.R.S.,

Professor of Chemistry in the University of Virginia.

(Continued from p. 128).

Sixth Series of Experiments.

THESE experiments consisted merely in the further application of electrolysis to the deposition of metallic gold from a solution of potassium auro-cyanide, comparing the weight of the metal thrown down, however, not with the weight of silver, but with the volume of hydrogen gas liberated by the action of the same current, the object being to thus secure, with an assumed knowledge of the density of hydrogen, a direct comparison of the atomic weight of gold with that of the element most generally taken as the basis of the numerical constants in question.

A cell containing the same solution of potassium auro-cyanide as was used in the fifth series of experiments, and having immersed in it a pair of plates of "proof" gold, as already described, was employed for the deposition of the gold. The same current which traversed this cell was passed through a hydrogen voltameter of special construction,† made of glass, in a single piece, the general character of which will be seen from Fig. 5.

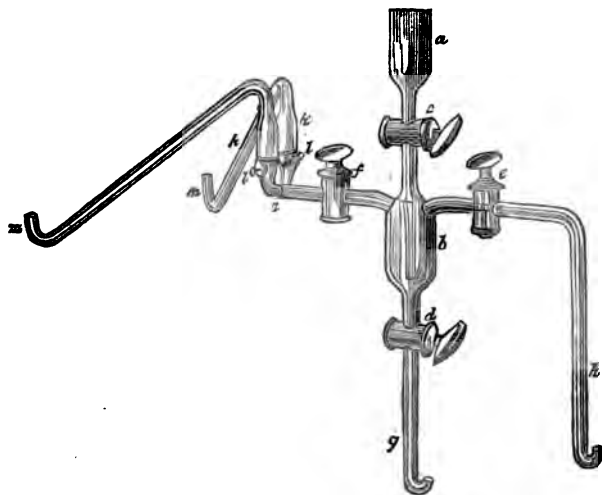
When this instrument was to be prepared for use, it was cautiously heated pretty strongly in an air-bath to remove the film of moisture and air from the internal surface, drawing dry air through by means of an aspirator. Clean mercury, previously heated, was then poured in through the funnel *a*, going down to nearly the bottom of the cylindrical vessel *b*, until this vessel—about 30 m.m. in diameter, and 60 m.m. in height—was completely filled, and also the tubes and stop-cocks, *c*, *d*, *e*, and *f*, each of these in succession being opened to allow escape of air, and afterwards closed; *f* was a three-way stop-cock, which could either be made to open communication between the parts of the tube on either side of it, or to simply close this tube, or to close this tube and establish communication between the vessel *b* and the outside air through the base of the stop-cock; it was in this last-named way that air and surplus mercury were allowed to escape, filling the tube between *b* and *f* with mercury, but not allowing of any of the metal going further along the tube towards *i*. The stop-cock *c* was closed, with the tube on which it was situated completely full with mercury, and leaving surplus mercury in the funnel *a*. In filling *b* and its connected tubes, care was taken to leave no visible bubbles of air. Pure water mixed with one-twelfth its weight of pure sulphuric acid was boiled for some time in a small flask, to dispel all dissolved air, keeping up the volume by additions from time to time of water kept boiling in a second flask; the lower turned-up end of the tube *h* was then immersed in the dilute acid, and the lower end of *g* in a cup of mercury; on opening the stop-cocks *e* and *d* mercury ran out from *g*, and the dilute acid came in

* A Paper read before the Royal Society, May 9, 1889.

† This piece of apparatus—an excellent specimen of skilful glass-blowing—was made, from drawings furnished by me, by Mr. Emil Greiner, 63, Maiden Lane, New York.

through *h*, filling about half-full the cylinder *b*. Closing *d* and *e*, opening *c*, and keeping up a supply of mercury in the funnel *a*, *f* was now turned so as to force out through the base of this stop-cock the little mercury in the tube behind it, and fill this tube with the acidulated water. Then *f* was turned so as to allow of this acidulated water being forced on to the bend, *i*, and into the two little voltameter tubes, *k* and *k*, filling these about one-third full. While these tubes were being thus filled, the extremities of the delivery tubes, *m* and *m*, were in communication with a Sprengel pump, so that they were very nearly exhausted of air. The stop-cock *f* having been closed, *e* was opened, and by suitable tilting of the apparatus, and running in of mercury from the funnel, *a*, nearly all of the acidulated water from *f* backwards was expelled through the tube *h*. A repetition of the procedure by which the cylinder, *b*, had been partially filled with acidulated water now served to partially fill it with well-boiled and still hot distilled water, to which no acid had been added. The two delivery tubes, *m* and *m*, were severally detached from the Sprengel pump, after allowing (by a special separate arrangement of tubes with stop-cocks) hydrogen to enter one of the two and oxygen the other, and when thus filled the ends of these two tubes

FIG. 5.

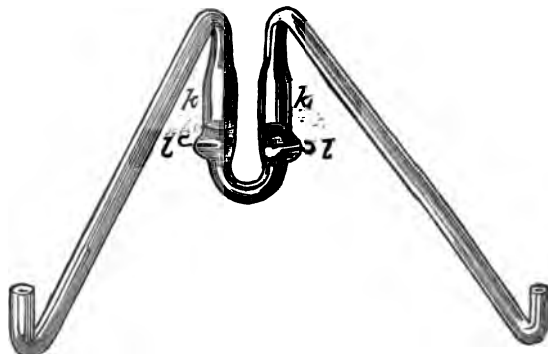


were dipped under mercury, and the two platinum wires *l* and *l*, sealed into the voltameter tubes were connected by the little rings on their outer ends with the terminals of the galvanic cells whence the electric current was to be derived, taking care, of course, to connect to the negative pole the wire of the tube already filled in its upper part with hydrogen, and to the positive pole the wire of the oxygen tube. Viewed from the front, the two voltameter and delivery tubes presented the appearance shown in Fig. 6. The little voltameter tubes, *k* and *k*, had an external diameter of about 12 m.m. and a length of 40 m.m. The platinum wires, *l* and *l*, serving as electrodes, were 1 m.m. in diameter, and extended beyond the interior surface of the glass (into which they were sealed) for only 3 m.m. in length. They could be well covered, and the voltameter tubes filled to one-third their capacity, with only about 2 c.m. of the acidulated water. By careful tilting of the apparatus laterally it was found to be possible to so regulate the pressure of mercury at the ends of the delivery tubes, and therefore the gaseous tension in the two voltameter tubes, that the acidulated water was not forced over from the one to the other, which, had it occurred, would have allowed admixture of the two gases; this required constant watching, however, and there was needed

from time to time a little tapping of the apparatus to get rid of the effect of irregular adhesion of the liquid to the walls of the voltameter tubes.

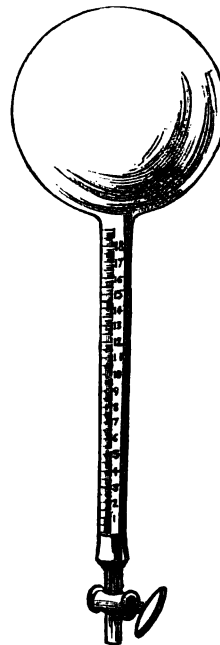
It will be seen that, with the arrangement described, the electrolysis could be effected of acidulated water, thoroughly deprived in advance of dissolved air, and in

FIG. 6.



quantity so small as to be capable of retaining in solution but infinitesimal quantities of the hydrogen and oxygen electrolytically separated. As the decomposition proceeded, the quantity of liquid in the voltameter tubes could be maintained constant by opening the stop-cock *c*, with a supply of mercury in the funnel *a*, and then cautiously opening *f*, so as to feed forward a little of the air-free water from the cylinder *b*, thus leaving the proportion of acid unaltered. The surface presented by the

FIG. 7.



platinum wire electrodes was so small as to allow of occlusion of the gases to only an extremely minute extent, and both the hydrogen and oxygen were allowed to escape for some time before any was collected for measurement.

The hydrogen only was collected and measured. I had hoped to apply this form of voltameter to a more exact

determination of the relative volumes of hydrogen and oxygen derived from water by electrolysis than is possible with the voltmeters of more common construction. But I have not yet seen my way to getting over the difficulties connected with the presence of ozone, hydrogen dioxide, Berthelot's per-sulphuric acid, or other by-products in the oxygen gas evolved at the positive pole. If this could be accomplished, a useful contribution might possibly be made to the question, revived and worked upon of late by several chemists, of the exact atomic weight of oxygen. The vessel for collecting and measuring the hydrogen, shown in Fig. 7, consisted of a spherical globe of tolerably stout glass, with a capacity of about 250 c.m., having a neck of about 1 c.m. internal diameter, and 22 c.m. long. This neck had etched upon it a simple linear scale of millimetres. At the mouth it was fitted with a well-ground perforated glass stopper, forming part of a glass stop-cock with an outer orifice of about 1 m.m. bore. The exact capacity of the whole globe and neck was ascertained by heating it in an air-bath to remove air and moisture condensed on the interior surface, drawing dry air through with an aspirator, then filling the globe with heated mercury, allowing it to cool to an accurately noted temperature, immersing the body of the globe in an outer vessel of mercury so as to prevent extension or flexure of the glass by the weight of the contained metal, filling up to the very mouth with mercury, inserting the stopper with the stop-cock open, thus forcing out through its orifice the last of the air, closing the stop-cock, removing from the orifice tube, by an iron wire, the drop or two of mercury remaining in it, and then emptying the flask, and carefully weighing in successive portions the mercury which it had held. The hydrogen from the voltmeter was collected in this flask, without its stopper, the flask having been previously filled with mercury, with the needful precautions for removal of all air, and inverted over a mercury trough. In each experiment the process of electrolysis was arrested when the hydrogen had filled the body of the globe and reached to a point rather more than half-way down the length of the neck, the gold plates being of course withdrawn at the same moment from their cell of gold solution, set away to soak in distilled water, and afterwards thoroughly washed, dried, heated in the Sprengel vacuum, cooled, and weighed. The portion of hydrogen collected was dried by successive balls of fused potash introduced and withdrawn by means of platinum wire. The neck of the flask having, in advance of the collection of hydrogen, been passed through a cork, this was used to close the mouth, placed downwards, of a vessel through which a stream of water was caused to flow rapidly from the pipes supplying the University buildings. The atmospheric temperature of the day on which the electrolysis experiment was made having been such as not to differ too much from the temperature of the water from the pipes, the gas occupied such a volume after equal exposure to this latter temperature that the mercury marked a point somewhere within the length of the neck, which point was noted by the millimetre scale, the thermometer immersed in the flowing water, and the barometer and its attached thermometer being read at the same time. It remained only to insert the stop-cock stopper under the mercury of the little mercury trough, close the stop-cock, withdraw the flask from the trough, reject the drop or two of mercury from the stopcock orifice by means of a wire, remove the portion of mercury left in the neck of the flask, and weigh it carefully. Its weight, with considera-

tion of its temperature when the stop-cock was closed, gave the volume of the portion of the flask not occupied by hydrogen, and this, subtracted from the whole volume of the interior of the flask, as found by the original calibration, gave the volume, under known conditions of temperature and pressure, of the hydrogen which had been collected. From two calibrations at different temperatures a correction was obtained for the expansion of the glass of the flask, but it was hardly necessary to take this into account, in view of the small limits within which temperature varied in all the experiments made.

But three experiments carried out by this method led to results which seemed worthy of confidence. These results were as in Table below.

In calculating the weight of hydrogen from its observed volume, Regnault's value for the weight of a litre of this gas at 0° C. and 760 m.m. was taken as the basis. The correction, of which Lord Rayleigh not long since pointed out the need—namely, for the compression of the vacuous glass flask by atmospheric pressure—was adopted from the experiments of J. M. Crafts (*Comptes Rendus*, vol. cvi., p. 1662); and his corrected value, 0.08988 grm., was still further corrected for the difference in the force of gravity at Paris and at the University of Virginia (in C.G.S. units, 980.94 : 979.95), giving as the value to be used 0.08979 grm.

The electrolysis of the water was carried on very slowly, so as to keep the density of the current low with such small electrodes as were used. Nevertheless, as the hydrogen voltmeter required constant watching, it became necessary to bring the whole time of an experiment within moderate limits, and hence a considerably stronger current was used than in the simultaneous deposition of gold and silver in the fifth series, this circumstance being less favourable to the satisfactory deposition of the gold. It would have been desirable to use a larger flask, and to collect a greater volume of hydrogen; but this, on account of the time required, would have made an experiment exceedingly troublesome and difficult.

In the work of this series the same unsatisfactory need for selecting only such results as came fairly close to the figures expected, and rejecting several others on the ground of very considerable departure therefrom, and the same sources of possible constant error in regard to the gold deposit present themselves which have already been noticed under the head of the fifth series. As regards the hydrogen, one is led to consider possible diffusion of hydrogen and oxygen between the two little voltmeter tubes, and slight imperfection in the drying of the hydrogen obtained. The former would, on the whole, probably tend to diminish the volume of gas collected, and hence to raise the apparent value of the atomic weight of gold. The latter would have the opposite tendency. That neither can have had more than an extremely minute influence was fairly proved by testing a part of the hydrogen obtained, on the one hand, by passing it through a red-hot glass tube, and on the other by submitting it to more extended drying by contact with phosphorus pentoxide both before and after such heating; in neither case was there appreciable change of volume.

Notwithstanding the desirability of comparing the atomic weight of any other element directly with that of hydrogen, the difficulty is not to be overlooked of doing this for an element having so high an atomic weight as that of gold. There is a manifest objection to the necessity of dealing with such minute quantities of hydrogen as those concerned in these experiments. A

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited. Grms.	Hydrogen liberated.	
				Vol. at 0° C. and 760 m.m. Cm.	Weight. Grm.
I.	A, b	C	4.0472	228.64	0.02053
II.	A, b	C	4.0226	227.03	0.02039
III.	A, b	C	4.0955	231.55	0.02079

very small error in the determination of the hydrogen greatly affects the value found for an atomic weight nearly two hundred times as large. It is true that the measurement of the volume of the hydrogen admits of being made with such precision as to leave room for but an extremely minute error in the corresponding weight, yet this measurement is not one of *limitless* delicacy, particularly if the difficulty be properly appreciated of ascertaining with certainty the precise temperature of the gas at the time its volume is read. Moreover, in measuring the volume of the gas, and thence deducing its weight, there is need not merely for a knowledge of changes of temperature and pressure, but for *absolutely* correct readings of the barometer and thermometer, so that there must usually be a degree of hesitation in accepting the readings of even fairly standard instruments, when temperature and pressure come to be placed in comparison with these conditions as affecting the results of Regnault for gaseous density. Nor can the results of that great physicist be assumed as themselves free from all possible need of further correction.

The error of direct comparison with so small an atomic weight as that of hydrogen is, however, after all only *masked* by substituting an *indirect* comparison through some larger atomic weight, since the assumed value of the latter is uncertain within limits which depend upon its comparison with the atomic weight of hydrogen.

(To be continued).

THE GLOW OF PHOSPHORUS.*

By Professor THORPE, F.R.S.

THE word *phosphorus* originally applied to any substance, solid or liquid, which had the property of shining in the dark, has gradually lost its generic sense, and is nowadays practically restricted, as a designation, to the wax-like inflammable substance which plays such an important part in the composition of an ordinary lucifer match. Phosphorus, indeed, is one of the most remarkable of the many remarkable substances known to the chemist. The curious method of its discovery, the universality of its distribution, its intimate connection with the phenomena of animal and vegetable life, its extraordinary physical properties and chemical activity, its abnormal molecular constitution, the protean ease of its allotropic transformations, all combine to make up a history which abundantly justifies its old appellation of the *phosphorus mirabilis*. Godfrey Hankewitz, more than 150 years ago, wrote:—"This phosphorus is a subject which occupies much the thoughts and fancies of some alchemists who work on microcosmical substances, and out of it they promise themselves golden mountains." Certainly no man of his time made more in the way of gold out of phosphorus than Mr. Hankewitz, for at his little shop in the Strand he enjoyed for many years the monopoly of its sale, guarding his *arcana* with all the jealousy of a modern manufacturer of the element.

Phosphorus, or, as it was then called, *noctiluca*, was first seen in this country in 1677. It was shown to Robert Boyle, who had already worked on phosphorescence in general, and who seems to have been specially struck with the remarkable peculiarity of a factitious body which could be made "to shine in the dark without having been before illumined by any lucid substance, and without being hot as to sense." In these respects the substance differed from all the *phosphori* hitherto known. The conditions which determine its glow were the subject of the earliest observations on phosphorus, and Boyle has left us a minute account of his work on the point. In the first place, he noticed that

the substance was only luminous in presence of air. He accurately describes the nature of the light, and noticed that "the water in which the phosphorus was partially immersed acquired a strong and penetrant taste, . . . and relished a little like vitriol. On evaporation it would not shoot into crystals, . . . but coagulated into a substance like a Gelly, or the Whites of Eggs, which would be easily melted by heat. On heating this 'Gelly' it gave off flashes of fire and light,' and had a 'garlick smell.'" He also found that the *noctiluca* was soluble in certain oils, and he particularly mentions oil of cloves as a convenient means of showing the luminosity as it is "rendered more acceptable to the standers-by by its grateful smell. In Oyl of Mace it did not appear luminous, nor in Oyl of Aniseeds." Boyle describes a number of experiments showing how small a quantity of the phosphorus is required to produce a luminous effect. "A grain of the *noctiluca* dissolved in Alkohol of Wine and shaken in Water; it render'd 400,000 times its weight luminous throughout. And at another Tryal I found that it impregnated 500,000 times its weight; which was more than one part of Cochineel could communicate its colour to. And one thing further observable was that when it had been a long time exposed to the air it emitted strong and odoriferous exhalations distinct from the visible fumes." The strong and odoriferous exhalations we now know to be ozone.

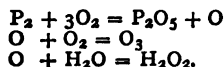
The earlier volumes of the *Philosophical Transactions of the Royal Society* contain several papers on the luminosity of phosphorus, and one by Dr. Frederic Slare is noteworthy, as giving one of the earliest, if not actually the earliest, account of what is one of the most paradoxical phenomena connected with the luminosity of phosphorus, namely, its increase on rarefying the air. "It being now generally agreed that the fire and flame [of phosphorus] have their pabulum out of the air, I was willing to try this matter *in vacuo*. To effect this, I placed a considerable lump of this matter (phosphorus) under a glass, which I fixed to an engine for exhausting the air; then presently working the engine, I found it grow lighter [*i.e.*, more luminous], though a charcoal that was well kindled would be quite extinguished at the first exhaustion; and upon the third or fourth draught, which very well exhausted the glass, it much increased in light, and continued so to shine with its increased light for a long time; on re-admitting the air, it returns again to its former dulness." This observation was repeated and its result confirmed by Hawksbee, in this country, and by Homberg, in France, and seems subsequently to have led Berzelius, and after him Marchand, to the conclusion that the luminosity of phosphorus was altogether independent of the air (*i.e.*, the oxygen), but was solely due to the volatility of the body. Many facts, however, combine to show that the air (oxygen) is necessary to the phenomenon. Lampadius found that phosphorus would not glow in the Torricellian vacuum, and Lavoisier, in 1777, showed that it would not inflame under the same conditions; and the subsequent experiments of Schrotter, Meissner, and Müller are decisive on the point that the glow is the concomitant of a chemical process dependent upon the presence of oxygen. It is, however, remarkable that phosphorus will not glow in oxygen at the ordinary atmospheric pressure and temperature, but that if the oxygen be rarefied the glow at once begins, but ceases again immediately the oxygen is compressed. Indeed, phosphorus will not glow in compressed air, and the flame of feebly burning phosphorus may be extinguished by suddenly increasing the pressure of the gas. Phosphorus, however, can be made to glow in oxygen at the ordinary pressure, or in compressed air if the gases be gently warmed. In the case of oxygen, the glow begins at 25° and becomes very bright at 36°. In compressed air the temperature at which the glow begins depends upon the tension. If the oxygen be absolutely deprived of moisture the phosphorus refuses to glow under any conditions. This fact, strange as it may seem, is not with-

* A Lecture delivered at the Royal Institution, on Friday, March 14, 1890.

out analogy; the presence of traces of moisture appears to be necessary for the initiation or continuance of chemical combination in a number of instances.

It was observed by Boyle that a minute quantity of the vapour of a number of essential oils extinguished the glow of phosphorus. The late Professor Graham confirmed and extended these observations; he showed that relatively small quantities of olefant gas and of the vapours of ether, naphtha, and oil of turpentine entirely prevented the glow, and subsequent observers have found that many essential oils, such as those of peppermint and lemon, and the vapours of camphor and asafetida, even when present in very small quantity, stop the absorption of oxygen, and the slow combustion of phosphorus in air.

It has been established that whenever phosphorus glows in air, or in rarefied oxygen, ozone and hydrogen peroxide are formed, but it is not definitely known whether the formation of these substances is the cause or the effect of the chemical process of which the glow is the visible sign. That there is some intimate connection between the luminosity of the phosphorus and the production of these bodies is highly probable. Schonbein, as far back as 1848, sought to demonstrate that the glow depends on the presence of ozone. It is certainly true that many of the substances, such as the essential oils, which prevent the glow of phosphorus, also destroy ozone. At a low temperature phosphorus produces no ozone in contact with air, neither does it glow. It has been found, in fact, that with air ozone is produced in largest quantity at 25°, at which temperature phosphorus glows brightly. On the assumption that the oxidation of the phosphorus consists in the immediate formation of the highest oxide, the production of the ozone and the hydrogen peroxide has been represented by the following equations:—



Both these reactions may, of course, go on simultaneously; ozone and hydrogen peroxide are not mutually incompatible; the synthesis of hydrogen peroxide by the direct oxidation of water seems to occur in a number of processes. But such symbolic expressions can at most be only very partial representations of what actually occurs. It is highly probable that the combination which gives rise to the glow only occurs between the vapour of phosphorus and the oxygen. Phosphorus is sensibly volatile at ordinary temperatures, and by rarefying the atmosphere in which it is placed its volatilisation is increased, which serves to account for the increased glow when the pressure of the gas is diminished. When phosphorus is placed in an atmosphere of hydrogen, nitrogen, or carbonic acid, these gases, when brought into contact with oxygen, become luminous from the oxidation of the vapour of phosphorus diffused through them. The rapidity of volatilisation varies with the particular gas; it is greatest in the case of hydrogen, and least in that of carbonic acid. Indeed, a stream of hydrogen gas at ordinary temperatures carries away comparatively large quantities of phosphorus, which may be collected by appropriate solvents. No ozone and no glow is produced in oxygen gas at ordinary temperatures and pressures, but on warming the oxygen both the ozone and the glow are formed. On passing ozone into oxygen at temperatures at which phosphorus refuses to glow, the phosphorus at once becomes luminous, oxygen is absorbed, and the characteristic cloud of oxide is produced, and the effect continues so long as the supply of ozone is maintained. A drop of ether at once extinguishes the glow.

Phosphorus combines with oxygen in several proportions, and the study of the mode of formation and properties of these oxides is calculated to throw light upon the nature of the chemical process which attends the glow of phosphorus.

Certain of these oxides have recently been the subject

of a considerable amount of study in the chemical laboratories of the Normal School of Science.

When phosphorus is slowly burned in air, there is produced a considerable quantity of a volatile substance having a characteristic garlic-like smell, which solidifies, when cooled, in beautiful arborescent masses of white crystals. It melts at about 23° and boils at 173°. In a sealed tube, kept in the dark, it may be preserved unchanged, but on exposure to light, and especially to bright sunshine, it rapidly becomes deep red. It slowly absorbs oxygen at the ordinary temperature and pressure, but from the mode in which the solid product of the reaction (P_2O_5) is deposited, it is evident that the union only takes place between the vapour of the oxide and the oxygen gas. Under diminished pressure the act of combination is attended with a glow, which increases in brilliancy if ozone be present. On compressing the oxygen the glow ceases. No ozone is formed during the act of oxidation. The degree of rarefaction needed to initiate the glow depends upon the temperature of the oxide; the warmer the oxide the less is the diminution of pressure required. By gradually warming the oxide the luminosity steadily increases, both in area and intensity, until at a certain temperature the mass ignites. The change from glow to actual flame is perfectly regular and gradual, and is unattended with any sudden increase in brilliancy. In this respect the process of oxidation is analogous to the slow and barely visible burning of fire-damp which is sometimes seen to occur in the Davy lamp, or to the slow combustion of ether and other vapours which has been specially studied by Dr. Perkin. Other instances of what may be called *degraded combustion* are known to chemists. Thrown into warm oxygen, the substance burns into flame at once and burns brilliantly, and it also takes fire in contact with chlorine. Alcohol also ignites it, and when it is warmed with a solution of potash it evolves spontaneously inflammable phosphoretted hydrogen. In contact with water it suffers only a very gradual change, and many days may elapse before even a comparatively small quantity is dissolved. This substance has long been known; it was discovered, in fact, by the French chemist Sage, but its true nature has only now been determined; its chemical formula is found to be P_4O_6 , hence its composition is similar to that of its chemical analogue, arsenious oxide.

The study of the properties of this remarkable substance enables us to gain a clearer insight into the nature of the chemical process attending the glow of phosphorus. When phosphorus is placed in oxygen, or in an atmosphere containing oxygen, under such conditions that it volatilises, the phosphorus oxidises, partly into phosphoric oxide and partly into phosphorous oxide. Ozone is formed, possibly by the reaction already indicated, and this reacts upon the residual phosphorus vapour and the phosphorus oxide, with the production of the luminous effect to which the element owes its name. The glow itself is nothing but a slowly burning flame, having an extremely low temperature, caused by the chemical union of oxygen with the vapours of phosphorus and phosphorous oxide. By suitable means this glow can be gradually augmented until it passes by regular gradation into the active vigorous combustion which we ordinarily associate with flame. Many substances, in fact, may be caused to phosphoresce in a similar way. Arsenic, when gently heated, glows in oxygen, and sulphur may also be observed to become luminous in that gas at a temperature of about 200°.

A Contribution to the Chemical Study of the Truffle.—Ad. Chatin.—The author determines the absolute weight of nitrogen, its proportion to the totality of the organic matter, the weight of the ash, and the proportion of each of the mineral elements. An analysis of the soils was carried on simultaneously. In the ash of the truffle the phosphoric acid ranges from 20 to 30 per cent.—*Comptes Rendus*, Vol. cx., No. 8.

SMOKELESS EXPLOSIVES.*

By Sir FREDERICK ABEL, C.B., D.C.L., D.Sc., F.R.S., V.P.R.I.

THE production of smoke which attends the ignition or explosion of gunpowder is often a source of considerable inconvenience in connection with its application to naval or military purposes, its employment in mines, and its use by the sportsman, although occasions not unfrequently arise during naval and military operations when the shroud of smoke produced by musketry or artillery fire has proved of important advantage to one or other, or to both, of the belligerents during different periods of an engagement.

Until within the last few years, however, but little, if any, thought appears to have been given to the possibility of dispensing with or greatly diminishing the production of smoke in the application of fire-arms, excepting in connection with sport. The inconvenience and disappointment often resulting from the obscuring effects of a neighbouring gun-discharge, or of the first shot from a double-barrel gun, led the sportsman to look hopefully to gun-cotton, directly after its first production in 1846, as a probable source of greater comfort and brighter prospects in the pursuit of his pastime and in his strivings for success.

A comparison between the chemical changes attending the burning, explosion, or metamorphosis of gun-cotton and of gunpowder, serves to explain the cause of the production of smoke in the latter case, and the reason of smokelessness in the case of gun-cotton. Whilst the products of explosion of the latter consist exclusively of gases and of water which assumes the transparent form of highly-heated vapour at the moment of its production, the explosive substances classed as gunpowder, composed of mixtures of saltpetre or another nitrate of a metal, with charred wood or other carbonised vegetable matter, and with variable quantities of sulphur, furnish products of which very large proportions are not gaseous, even at high temperatures. Upon the ignition of such a mixture, these products are in part deposited in the form of a fused residue, which constitutes the fouling in a fire-arm, and are in part distributed, in an extremely fine state of division, through the gases and vapours developed by the explosion, thus producing smoke.

In the case of gunpowder of ordinary composition, the solid products amount to over fifty per cent by weight of the total products of explosion, and the dense white smoke which it produces consists in part of extremely finely divided potassium carbonate, which is a component of the solid products, and, to a great extent, of potassium sulphate, produced chiefly by the burning of one of the important solid products of explosion—potassium sulphide—when it is carried in a fine state of division into the air by the rush of gas.

With other explosives, which are also smoke-producing, the formation of the smoke is due to the fact that one or other of the products, although existing as vapour at the instant of its development, is immediately condensed to a cloud composed of minute liquid particles or of vesicles, as in the case of mercury vapour liberated upon the explosion of mercuric fulminate, or of the aqueous vapour produced upon the ignition of a mixture of ammonium nitrate and charcoal, or ammonium nitrate and picric acid.

Until within the last half-dozen years, the varieties of gunpowder which have been applied to war purposes in this and other countries have exhibited comparatively few variations in chemical composition. The proportions of charcoal, saltpetre, and sulphur, employed in their production, exhibit slight differences in different countries, and these, as well as the character of the charcoal used, its sources and method of production, underwent but

little modification for very many years. The same remark applies to the nature of the successive operations pursued in the manufacture of black powder for artillery purposes in this and other countries.

The replacement of smooth-bore guns by rifled artillery, which followed the Crimean war, and the increase in the size and power of guns consequent upon the application of armour to ships and forts, soon called for the pursuit of investigations, having for their object the attainment of means for variously modifying the action of fired gunpowder, so as to render it suitable for the different calibres of guns, whose full power could not be effectively, or in some instances safely, developed by the use of the kind of gunpowder previously employed indiscriminately in artillery of all known calibres.

In order to control the violence of explosion of gunpowder, by modifying the rapidity of transmission of explosion from particle to particle, or through the mass of each individual particle, of which the charge of a gun is composed, the accomplishment of the desired results was, in the first instance, and indeed throughout practical investigations extending over many years, sought exclusively in modifications of the size and form of the individual masses composing a charge of powder, and of their density and hardness; it being considered that, as the proportions of saltpetre, charcoal, and sulphur, generally employed in the production of gunpowder, very nearly correspond to those required for the development of the greatest chemical energy by those incorporated materials, it was advisable to seek for the attainment of the desired results by modifications of the physical and mechanical characters of gunpowder, rather than by any modification in the proportions and chemical characters of its ingredients.

The varieties of powder, which, as the outcome of careful, practical, and scientific researches in this direction, have been introduced into artillery service from time to time, and some of which, at any rate, have proved fairly efficient, have been of two distinct types. The first of these, produced by breaking up more or less highly-pressed cakes of black powder into grains, pebbles, or boulders of approximately uniform size and shape, the sharp edges and rough surfaces being afterwards removed by attrition (reeling and glazing), are simply a further development of one of the original forms of granulated or corned powder, represented by the old F. G., or small arms and L. G., or cannon powder. Gunpowders of this class, ranging in size from about 1000 pieces to the ounce to about six pieces to the pound, have been introduced into artillery service, and certain of them, viz., R. L. G. (rifle large grain), which was the first step in advance upon the old cannon powder (L. G.), pebble powder (P), and large pebble or boulder powder (P 2), are still employed more or less extensively in some guns of the present day.

The other type of powder has no representative among the more ancient varieties; it has its origin in the obviously sound theoretical view that uniformity in the results furnished by a particular powder, when employed under like conditions, demands not merely identity in regard to composition, but also identity in form, size, density, and structure of the individual masses composing the charge used in a gun. The practical realisation of this view should obviously be attained, or at any rate approached, by submitting equal quantities of one and the same mixture of ingredients, presented in the form of powder of uniform fineness and dryness to a uniform pressure for a fixed period in moulds of uniform size, and under surrounding conditions as nearly as possible alike. The fulfilment of these conditions would, moreover, have to be supplemented by an equally uniform course of proceeding in the subsequent drying and other finishing processes to which the powder masses would be submitted.

The only form of powder, introduced into our artillery service for a brief period, in the production of which

* A Lecture delivered before the Royal Institution of Great Britain, Friday, January 31, 1890.

these conditions were adhered to as closely as possible, was a so-called pellet powder, which consisted of small cylinders, having semi-perforations with the object of increasing the total inflaming surface of the individual masses.

Practical experience with this powder, and with others prepared upon the same system, but with much less rigorous regard to uniformity in such details as state of division and condition of dryness of the powder before its compression into cylindrical or other forms, showed that uniformity in the ballistic properties of black powder could be as well and even more readily secured by the thorough blending or mixing together of batches presenting some variation in regard to density, hardness, or other features, as by aiming at an approach to absolute uniformity in the characters of each individual mass composing a charge.

At the time that our attention was first actively given to this subject of the modification of the ballistic properties of powder, it had already been to some extent dealt with in the United States by Rodman and Doremus, and the latter was the first to propose the application, as charges for guns, of powder masses produced by the compression of coarsely grained powder into moulds of prismatic form. In Russia the first step was taken to utilise the results arrived at by Doremus, and to adopt a prismatic powder for use in guns of large calibre.

Side by side with the development and perfection of the manufacture of prismatic powder in Russia, Germany, and in this country, new experiments on the production of powder masses suitable, by their comparative gradual action, for employment in the very large charges required for the heavy artillery of the present day, by the powerful compression of mixtures of more or less finely broken up powder-cake into masses of greater size than those of the pebble, pellet, and prism powders, were actively pursued in Italy, and also by our own Government Committee on Explosives, and the outcome of very exhaustive practical investigations were the very efficient Fossano powder, or *poudre progressif*, of the Italians, and the boulder and large cylindrical powders known as P* and C*, produced at Waltham Abbey, which scarcely vied, however, with the Italian powder in the uniformity of their ballistic properties.

Researches carried out by Captain Noble and the lecturer some years ago with a series of gunpowders differing considerably in composition from each other, indicated that advantages might be secured in the production of powders for heavy guns by so modifying the proportions of the constituents (*e.g.*, by considerably increasing the proportion of charcoal and reducing the proportion of sulphur) as to give rise to the production of a much greater volume of gas, and at the same time to diminish the heat developed by the explosion.

These researches served, among other purposes, to throw considerable light upon the cause of the wearing or erosive action of powder-explosions upon the inner surface of the gun, which in time produces so serious a deterioration of the arm that the velocity of projection and accuracy of shooting suffer very greatly, an effect, the extent of which increases in an increasing ratio to the size of the guns in consequence, obviously, of the large increase in the weight of the charges fired.

Several causes undoubtedly combine to bring about the wearing away of the gun's bore, which is especially great where the products of explosion, while under the maximum pressure, can escape between the projectile and the bore. The great velocity with which the very highly heated gaseous and liquid (fused solid) products of explosion sweep over the heated surface of the metal, gives rise to a displacement of the particles composing it, which increases as the surface becomes roughened by the first action upon the least compact portions of the metal, and thus opposes greater resistance; at the same time, the effect of the high temperature to which the surface is raised is to reduce its rigidity and power of resisting the

force of the gaseous torrent, and lastly some amount of chemical action upon the metal by certain of the highly heated non-gaseous products of explosion, contributes towards an increase in the erosive effects. A series of careful experiments made by Captain Noble with powders of different composition, and with other explosives, afforded decisive evidence that the explosive agent which furnished the largest proportion of gaseous products, and the explosion of which was attended by the development of the smallest amount of heat, exerted least erosive action.

It is probable that important changes in the composition of powders manufactured by us for our heavy guns would have resulted from those researches, but in the meantime, two eminent German gunpowder manufacturers had occupied themselves independently and simultaneously with the important practical question of producing some more suitable powder for heavy guns than the various new forms of ordinary black powder, the rate of burning of which, especially when confined in a close chamber, was, after all, reduced only in a moderate degree by the increase in the size of the masses, and by such increase in their density as it was practicable to attain. The German experimenters directed their attention not merely to an alteration of the proportions of the powder ingredients, but also to a modification in the character of charcoal employed, and the success attending their labours in these directions led to the practically simultaneous production, by Mr. Heidemann at the Westphalian Powder Works, and Mr. Düttenhofer at the Rottweil Works, near Hamburg, of a prismatic powder of cocoa-brown colour, consisting of saltpetre in somewhat higher proportion, of sulphur in much lower proportion than in normal black powder, and of very slightly burned charcoal, similar in composition to the charcoal (*charbon roux*) which Violette, a French chemist, first produced in 1847 by the action of superheated steam upon wood or other vegetable matter, and which he proposed for employment in the manufacture of sporting powder. These brown prismatic powders (or "cocoa powders," as they were termed from their colour) are distinguished from black powder, not only by their appearance, but also by their very slow combustion in open air, by their comparatively gradual and long-sustained action when used in guns, and by the simple character of their products of explosion as compared with those of black powder. As the oxidising ingredient, saltpetre, is contained, in brown or cocoa powder, in larger proportion relatively to the oxidisable components, sulphur and charcoal, than in black powder, these become fully oxidised, while the products of explosion of the latter contain, on the other hand, larger proportions of unoxidised material or of only partially oxidised products. Moreover, there is produced upon the explosion of brown powder a relatively very large amount of water-vapour, not merely because the finished powder contains a larger proportion of water than black powder, but also because the very slightly charred wood or straw used in the brown powder is much richer in hydrogen than black charcoal, and therefore furnishes by its oxidation a considerable amount of water. The total volume of gas furnished by the brown powder (at 0° C. and 760 m.m. barometer) is only about 200 volumes per kilogramme of powder, against 278 volumes furnished by a normal sample of black powder, but the amount of water-vapour furnished upon its explosion is about three times that produced from black powder, and this would make the volume of gas and vapour developed by the two powders about equal if the heat of its explosion were the same in the two cases; the actual temperature produced by the explosion of brown powder is, however, somewhat the higher of the two.

Although the smoke produced upon firing a charge of brown powder from a gun appears at first but little different in denseness to that of black powder, it certainly disperses much more rapidly, a difference which is probably due to the speedy absorption, by solution, of the

finely divided potassium salts by the large proportion of water-vapour distributed throughout the so-called smoke.

This class of powder was substituted with considerable advantage for black powder in guns of comparatively large calibre; nevertheless, it became desirable to attain even slower or more gradual action in the case of the very large charges required for guns of the heaviest calibres, such as those which propel shot of about 2000 lbs. weight. Accordingly, the brown powder has been modified in regard to the proportions of its ingredients to suit these conditions, while, on the other hand, powder intermediate with respect to rapidity of action between black pebble powder and the brown powder has been found more suitable than the former for use in guns of moderately large calibre.

The recent successful adaptation of machine guns and comparatively large quick-firing guns to naval service, more especially for the defence of ships against attack by torpedo boats, &c., has rendered the provision of a powder for use with them, which would produce comparatively little or no smoke, a matter of very considerable importance, inasmuch as the efficiency of such defence must be greatly diminished by the circumstance that, after a very brief use of the guns with black powder, the objects against which their fire is destined to operate become more or less completely hidden from those directing them by the dense veil of powder-smoke produced. Hence much attention has been directed during the last few years to the production of smokeless, or nearly smokeless, powders for naval use in the above directions. At the same time, the views of many military authorities regarding the importance of dispensing with smoke in land engagements has also created a demand, the apparent urgency of which has been increased by various circumstances, for a smokeless powder suitable for field artillery and small arms.

The properties of ammonium nitrate, of which the products of decomposition by heat are, in addition to water-vapour, entirely gaseous, have rendered it a tempting material to work upon in the hands of those who have striven to produce a smokeless powder; but its deliquescent character has been the chief obstacle to its application as a component of an explosive agent susceptible of substitution for black powder for service purposes.

A German chemical engineer, F. Gäns, conceived that, by incorporating charcoal and saltpetre with a particular proportion of ammonium nitrate, he had produced an explosive material which did not partake of the hygroscopic character common to other ammonium nitrate mixtures, and that by its explosion the potassium in the saltpetre formed a volatile combination with nitrogen and hydrogen, a *potassium amide*, so that, although containing nearly half its weight of potassium salt, it would furnish only volatile products. The views of Mr. Gäns regarding the changes which his so-called *amide powder* undergoes upon explosion were not borne out by existing chemical knowledge, while the powder compounded in accordance with his views proved to be by no means smokeless, and was certainly not non-hygroscopic. Mr. Heidemann has, however, been successful, by modifications of Gäns' prescription and by application of his own special experience in power-manufacture, in producing an ammonium nitrate powder possessed of remarkable ballistic properties, furnishing comparatively little smoke, which speedily disperses, and exhibiting the hygroscopic characteristics of ammonium nitrate preparations in a decidedly less degree than any other hitherto prepared. The powder, while yielding a very much larger volume of gas and water-vapour than black or brown powder, is considerably slower than the latter; the charge required to produce equal ballistic results is less, while the chamber-pressure developed is lower, and the pressures along the chase of the gun are higher, than in the case of brown powder.

The ammonium nitrate powder contains, in its normal dried condition, more water than even brown powder; it does not exhibit any great tendency to absorb moisture

from an ordinarily dry or even a somewhat moist atmosphere, but if the amount of atmospheric moisture approaches saturation it will rapidly absorb water, and when once the process begins it continues rapidly, the powder masses becoming speedily quite pasty. The charges for quick-firing guns are enclosed in metal cases, in which they are securely sealed up; the powder is therefore prevented from absorbing moisture from the external air, but it has been found that if the cartridges are kept for long periods in ship's magazines, in which, from their position relatively to the ship's boilers, the temperature is more or less elevated, sometimes for considerable periods, the expulsion of water from some portions of the powder-masses composing the hermetically sealed charge, and its constant irregular distribution, may give rise to a want of uniformity in the action of the powder, and to the occasional development of high pressures. Although, therefore, this ammonium nitrate powder may be regarded as the first successful advance towards the production of a comparatively smokeless artillery-powder, it is not uniformly well adapted to the requirements which it should fulfil in naval service.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 28TH, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, March 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from February 1st to February 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Excepting two samples which were recorded as "very slightly turbid," the whole of the 168 samples examined were found to be clear, bright, and well filtered.

Judged by the determinations of colour-tint, and of oxygen required for oxidation, the character of the water-supply to the Metropolis during the month of February has scarcely differed appreciably from that manifested during the previous months of December and January. But the proportion of organic carbon found in the water, though still low, both absolutely and in regard to the period of the year, has not continued to be of the exceptional degree of lowness for the season taken note of in our reports for the previous two months. As regards the Thames-derived supply, the mean proportion of organic carbon was found to be 0.160 part in 100,000 parts of the water, with a maximum of 1.74 part in any single sample examined, this maximum proportion of organic carbon

corresponding to about three-tenths of a grain of organic matter in 70,000 grains, i.e., a gallon of the water.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

CORRESPONDENCE.

SULPHIDE OF ANTIMONY.

To the Editor of the Chemical News.

SIR,—Having precipitated Sb as Sb_2S_3 in order to expel H_2S , I passed a current of CO_2 through the solution, and found, about three or four hours afterwards, that no precipitate was visible, the Sb_2S_3 being apparently dissolved in aqueous solution of CO_2 . On boiling the solution no precipitate came down, but on again passing H_2S through the liquid the Sb came down as Sb_2S_3 (the red variety), and, on filtration, it was found that there was still some of the Sb in solution as Sb_2S_3 , which came down when separated from the Sb_2S_3 .

This may prove a useful reaction in the separation of the second group sulphides.—I am, &c,

Claremont, Grove Road, Woodford,
Essex, March 16, 1890.

G. W. ENGLAND.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 8, February 24, 1890.

Composition of the Linear Spectra of the Chemical Elements.—J. R. Rydberg.—The author's researches have, so far, extended only to the Group I., II., and III. of the Periodic System. He designates by $n = 10^8 \lambda^{-1}$ (λ being expressed in Angström units) the number of waves in 1 c.m. of air. His conclusions are:—(1) The long rays form double or triple rays defined by the property that the difference (ν) of the number of waves of the corresponding components is constant in each element. (2) The corresponding components of the double or triple rays form series, the terms of which are functions of consecutive whole numbers. Each series may be approximately expressed by an equation of the form—

$$n = n_0 - \frac{N_0}{(m + \mu)^2}.$$

Here n is the number of waves, m any whole number whatever (the number of the order of the term), $N_0 = 109721.6$, a constant common to all the series and to all the elements, n_0 , μ , are specific constants of the series. (3) The different series of one and the same group (nebulous or narrow) have the same value of μ ; the difference of the values of $n_0 = \nu$. The series of the same number of order in the different groups have the same value of n_0 ; they are distinguished by the values of μ . (4) The wave-lengths of the corresponding rays, the same as the values of the constants ν , n_0 , μ in the corresponding series of the different elements are periodic functions of the atomic weight. The periodicity of the constants renders it possible to calculate by interpolation the spectrum of an element if we know the spectra of the adjoining

elements in the periodic system. The hypotheses of Mr. Lockyer on the Dissociation of the Elements are quite incompatible with the results of these investigations.

Vapour-Tension of Solution made in Acetic Acid.—F. M. Raoult and A. Recoura.—In all probability, at a given temperature the constitution of the physical molecule of a body is the same in the liquid state and in that of a saturated vapour.

The Action, in the Dry Way, of the Different Potassium and Sodium Arseniates upon the Oxides of the Magnesian Series.—C. Lefèvre.—The oxides of the magnesian series always give with the potassium arseniates, as final products, a double arseniate of the composition $2MO.KO.AsO_5$, thus behaving like the earthy-alkaline metals. With the sodium arseniates some give a double arseniate of a composition similar to the above; the others yield another double salt, poorer in oxide $Mo.2NaO.AsO_5$. The first series includes magnesium, zinc, and nickel; the second, cobalt, manganese, and cadmium.

The Volumetric Determination of Copper.—A. Etard and P. Lebeau.—(See p. 137).

Preparation of Hydroxycamphocarbonic Acid, setting out from Camphocarbonic Acid.—A. Haller and M. Minquin.—Not adapted for useful abstraction.

A New Putrefaction-Ptomaine obtained by the Culture of Bacterium Allii.—A. B. Griffiths.—The microbe concerned is chromogenous, producing a green pigment on the surface of putrid onions. The pigment is soluble in alcohol, and the solution gives an absorption spectrum consisting of a band which extends from the extreme violet to the blue (almost to the line F of the solar spectrum). There is also an absorption band in the green and one in the yellow. The end of the latter coincides with the line D. The ptomaine is a white solid, soluble in hot water, alcohol, ether, and chloroform. From water it crystallises in microscopic prismatic needles, very deliquescent. It gives with sodium phosphomolybdate a white precipitate; with iodine dissolved in potassium iodide, a maroon; with Nessler's solution, a yellowish maroon; with tannin, a maroon; with picric acid, a yellow; with gold chloride, a dense yellow; sulphuric acid, slightly diluted, gives a violet-red colour. The base forms a yellow crystalline chloroplatinate. The analysis of the base leads to the formula $C_{10}H_{17}N$. It is still uncertain whether it ought to be attached to pyridin or to the series $C_n H_{2n-5} N$.

Chromogenous Functions of the Pyrocyanic Bacillus.—C. Gessard.—The chromogenous function of this bacillus varies with the medium.

Bulletin de la Société Chimique de Paris. Series 3, Vol. iii., No. 1.

Observations on a New Method of Analysis, applicable to Industrial Water and to Water used for Feeding Steam-Boilers.—Leo Vignon.—The author refers to two earlier papers describing his method of analysis. He determines the carbonic acid volumetrically in a known volume of water by means of a standard solution of lime, using phenolphthalein as indicator. He then determines directly the quantity of sodium carbonate necessary to transform the calcium and magnesium chlorides and sulphates into the corresponding sodium salts. This result is obtained by adding to the water (which must be previously boiled to expel its free or semi-combined carbonic acid) a standard solution of sodium carbonate. Phenolphthalein is used as an indicator. In both operations colorimetric comparisons are made with distilled water. The author now adds the precaution that the distilled water used for comparison must have been recently boiled. Further, to expel the free carbonic acid

from the sample it is better to boil it in a porcelain or platinum vessel (not in glass) rather than use the lime-water.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Dynamite.—Would any of your readers inform me the best published work on the manufacture of dynamite?—"EXPLOSIVES."

MEETINGS FOR THE WEEK.

- MONDAY, 24th.**—Medical, 8.30.
Society of Arts, 8. "Some Considerations Concerning Colour and Colouring," by Prof. A. H. Church, M.A., F.R.S.
- TUESDAY, 25th.**—Royal Institution, 3. "The Post-Darwinian Period," by Prof. G. J. Romanes, M.A., LL.D., F.R.S.
Society of Arts, 8. "Engraving in Wood, Old and New," by W. J. Linton.
Institute of Civil Engineers, 8.
Royal Medical and Chirurgical, 8.30.
- WEDNESDAY, 26th.**—Society of Arts, 8. "Carriage-building and Street Traffic in England and France," by G. N. Hooper.
Geological, 8.
- THURSDAY, 27th.**—Royal, 4.30.
Chemical, 8. (Anniversary).
Institute of Electrical Engineers, 8.
Royal Institution, 3. "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations), by Frederick Niecks.
- FRIDAY, 28th.**—Royal Institution, 9. "Foam," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
Quekett, 8.
- SATURDAY, 29th.**—Royal Institution, 3. "Electricity and Magnetism," by Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S.
Society of Arts, 3. "The Atmosphere," by Prof. Vivian Lewes.

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THE CHEMICAL NEWS.

Vol. LXI. No. 1583.

SMOKELESS EXPLOSIVES.*

By Sir FREDERICK ABEL, C.B., D.C.L., D.Sc., F.R.S., V.P.R.I.

(Concluded from p. 144).

ATTENTION was first seriously directed to the subject of smokeless powder by the reports received about four years ago of remarkable results stated to have been obtained in France with such a powder for use with the magazine rifle (the Lebel) which was being adapted to military service. These Reports were speedily followed by others, descriptive of marvellous velocities obtained with small charges of this powder, or some modifications of it, from guns of very great length. As in the case of melinite, the fabulously destructive effects of which were much vaunted at about the same time, the secret of the precise nature of the smokeless powder was so well preserved by the French authorities, that surmises could only be made on the subject, even by those most conversant with these matters. It is now well known, however, that more than one smokeless explosive has succeeded the original powder, the perfection of which was reported to be beyond dispute, and that the material now adopted for use in the Lebel rifle bears, at any rate, great similarity to preparations which have been made the subject of patents in this country, and which are still experimental powders in other countries.

So far as smokelessness is concerned, no material can surpass *gun-cotton* pure and simple; but, even if its rate of combustion in a firearm could be controlled with certainty and uniformity, although only used in very small charges, such as are required for military rifles, its application as a safe and reliable propulsive agent for military and naval use is attended by so many difficulties, that the non-success of the numerous attempts, made in the first twenty-five years of its existence, to apply it in this direction, is not surprising.

Soon after its discovery by Schönbein and Böttger in 1846, endeavours were made to apply gun-cotton wool, rammed into cases, as a charge for small arms, but with disastrous results. Subsequently von Lenk, who made the first practical approach to the regulation of the explosive power of gun-cotton, produced small arm cartridges by superposing layers of gun-cotton threads, these being closely plaited round a core of wood. Von Lenk's system of regulating the rapidity of burning of gun-cotton, so as to suit it either for gradual or violent action, consists, in fact, in converting coarse or fine, loosely or tightly twisted, threads or rovings of finely carded cotton into the most explosive form of gun-cotton, and of arranging these threads or yarns in different ways, so as to modify the mechanical condition, i.e., the compactness and extent and distribution of enclosed air-spaces, of the mass of gun-cotton composed of them. Thus, small arm cartridges were composed, as already stated, of compact layers of tightly-plaited fine gun-cotton thread; cannon cartridges were made up of coarse loose gun-cotton yarn wound very compactly upon a core; charges for shells consisted of very loose cylindrical hollow plaits (like lamp wicks) along which fire flashed almost instantaneously; and mining charges were made in the form of a very tightly twisted rope with a hollow core. While the two latter forms of gun-cotton always burned with almost instantaneous rapidity in open air, and with highly destructive effects if they were strongly confined, the tightly wound or plaited masses burned slowly in air, and

would frequently exert their explosive force so gradually when confined in a firearm, as to produce good ballistic results without appreciably destructive effect upon the arm. Occasionally, however, in consequence of some slight unforeseen variation in the compactness of the material, or in the amount and disposition of the air-spaces in the mass, very violent action would be produced, showing that this system of regulating the explosive force of gun-cotton was quite unreliable.

Misled by the apparently promising nature of the earliest results which von Lenk obtained, the Austrian Government embarked, in 1862, upon a somewhat extensive application of von Lenk's gun-cotton to small-arms, and provided several batteries of field guns for the use of this material. The abandonment of these measures for applying a smokeless explosive to military purposes soon followed upon the attainment of unsatisfactory results, and was hastened by the occurrence of a very destructive explosion at gun-cotton stores at Simmering, near Vienna, in 1862.

It was at about this time that the attention of the English Government, and through them of the lecturer, was directed to the subject of gun-cotton, the Austrian Government having communicated details regarding improvements in its manufacture accomplished by von Lenk, and results obtained in the extended experiments which had been carried out on its application to the various purposes above indicated, according to the system devised by that officer. One of the results of the lecturer's researches, subsequently carried on at Woolwich and Waltham Abbey, was his elaboration of the system of manufacture and employment of gun-cotton which has been in extensive use at the government works with little, if any, modification for over eighteen years, and has been copied from us by France, Germany, and other countries. By reducing the partially purified gun-cotton-fibre to pulp, as in the ordinary process of making paper, completing its purification when in that condition, and afterwards converting the finely-divided explosive into highly compressed homogeneous masses of any desired form and size, very important improvements were effected in its stability, its uniformity of composition and action, and its adaptability to practical uses, a great advance being made in the exercise of control over the rapidity of combustion or explosion of the material.

No success had attended the experiments instituted in England with wound cannon cartridges of gun-cotton threads made according to von Lenk's plan; on the other hand, a number of results which at first sight appeared very promising were obtained at Woolwich in 1867-8 with bronze field-guns and cartridges built up of compressed gun-cotton masses arranged in different ways (with varied air-spaces, &c.) with the object of regulating the rapidity of explosion of the charge. But although the attainment of high velocities with comparatively small charges of the material, unaccompanied by any indications of injury to the gun, was frequent, it became evident that the fulfilment of the conditions essential to safety to the arm were exceedingly difficult to obtain with certainty; they appeared, indeed, to be altogether beyond absolute control, even in so small a gun as the twelve-pounder. Military authorities not being, in those days, alive to the advantages which might accrue from the employment of an entirely smokeless explosive in artillery, the lecturer received no encouragement to persevere with experiments in this direction, and the same was the case with respect to the possible use of a smokeless explosive in military small arms, with which, however, far more promising results had at that time been obtained at Woolwich.

Abel's system of preparing gun-cotton was no sooner elaborated than its application to the production of smokeless cartridges for sporting purposes was achieved with considerable success by Messrs. Prentice of Stowmarket. The first gun-cotton cartridge, which found considerable favour with sportsmen, consisted of a roll of

* A Lecture delivered before the Royal Institution of Great Britain, Friday, January 31, 1890.

felt-like paper composed of gun-cotton and ordinary cotton, and produced from a mixture of the pulped materials. Afterwards a cylindrical pellet of slightly compressed gun-cotton pulp was used, the rapidity of explosion of which was retarded, while it was at the same time protected from absorption of moisture by impregnation with a small proportion of indiarubber. Neither of these cartridges afforded promise of sufficient uniformity of action to fulfil military requirements, but after a series of experiments which the lecturer made with compressed gun-cotton arranged in various ways, very promising results were attained, especially with the Martini-Henry rifle and a charge of pellet-form, the rapidity of explosion of which was regulated by simple means.

A sporting powder which was nearly smokeless had, in the meantime, been produced by Colonel Schultze, of the Prussian Artillery, from wood cut up into very small cube-like fragments, converted into a mild form of nitro-cellulose after a preliminary purifying treatment, and impregnated with a small portion of an oxidising agent. Subsequently the manufacture of the Schultze powder was considerably modified; it was converted into the granular form and rendered considerably more uniform in character and less hygroscopic, and it then bore considerable resemblance to the E.C. powder, a granulated nitro-cotton powder, produced, in the first instance at Stowmarket, and consisting of a less highly nitrated cotton than gun-cotton (trinitro-cellulose), incorporated in the pulped condition with a somewhat considerable proportion of the nitrates of potassium and barium, and converted into grains through the agency of a solvent and a binding material. Both of these powders produced some smoke when fired, though the amount was small in comparison with that from black powder. They did not compete with the latter in regard to accuracy of shooting, when used in arms of precision, but they are interesting as being the forerunners of a variety of so-called smokeless powders, of which gun-cotton or some form of nitro-cellulose is the basis, and of which those of Johnson and Borland, and of the Smokeless Powder Company, are the most prominent in this country.

In past years, both camphor and liquid solvents, such as acetic ether and acetone, for gun-cotton, and mixtures of ether and alcohol for nitro-cotton, have been applied to the hardening of the surfaces of compressed masses or granules of those materials, by von Förster and others, with a view to render them non-porous, and in the E.C. powder manufacture the latter solvent was thus applied to harden the powder-granules. In the Johnson-Borland powder, camphor is applied to the same purpose; in smokeless powders of French and German manufacture acetic ether and acetone have been used, and the solvent has been applied, not merely to harden the granules or tablets of the explosive, but to convert the latter into a homogeneous horn-like material.

Much mystery has surrounded the nature and origin of the first smokeless powder adopted, apparently with undue haste, by the French Government, for use with the Lebel magazine rifle. A few particles of the Vieille powder, or *Poudre B*, were seen by the lecturer about two years ago, and very small specimens appear to have fallen into the hands of the German Government about that time. They were in the form of small yellowish brown tablets of about 0.07 inch to 0.1 inch square, of the thickness of stout note-paper, and had evidently been produced by cutting up thin sheets of the material. They appear to contain, as an important ingredient, picric acid (the basis of "mélinite") a substance extensively used as a dye, and obtained by the action of nitric acid, at a low temperature, upon carbolic acid and cresylic acid, constituents of coal tar. Originally produced by the action of nitric acid upon indigo, and afterwards by similar treatment of Botany Bay gum, it was first known as carbazotic acid, and is one of the earliest of known explosives of organic origin. When sufficiently heated, or when set light to, it burns with a yellow smoky flame, and even very large

quantities of it have been known to burn away somewhat fiercely, but without exploding. Under certain conditions, however, and especially if subjected to the action of a powerful detonator, it explodes with very great violence and highly destructive effects, as pointed out by Sprengel, in 1873, and recent experiments at Woolwich have shown that it does this even, as in the case of gun-cotton, when it contains as much as 15 per cent of water. It is no longer a secret that picric acid at any rate forms the basis of the much-vaunted and mysterious explosive for shells for which the French Government were said to have paid a very large sum of money, and the destructive effects of which have been described as nothing less than marvellous. M. Turpin patented, in 1875, the use of picric acid alone as an explosive for shells and for other engines of destruction, and whether or not his claims to be the inventor of mélinite are valid, there appears no doubt that his patent in France was the starting-point of the development and adoption of that explosive.

The attention thus directed in France to the properties of picric acid appears to have given rise to experiments resulting in its employment as an ingredient of the first smokeless powder (*Poudre B*) adopted for the French magazine rifle.

The idea of employing picric acid preparations as explosive agents for propulsive purposes originated with Designolle about twenty years ago, but no useful results attended the experiments with the particular mixtures proposed by him. It is certain that the recent adaptation of that substance in France was of a different character, and that, promising as were the results of the new smokeless powder, of which it appears to have formed an ingredient, and a counterpart of which was made the subject of experiments at Woolwich about three years ago, its deficiency in the all-essential quality of stability must have been, at any rate, one cause of its abandonment in favour of another form of smokeless powder, which there is reason to believe is of more simple character.

In Germany, the subject of smokeless powder for small arms and artillery was being steadily pursued in secret, while the sensational reports concerning *Poudre B* were spread about in France, and a small-arm powder giving excellent results in regard to ballistic properties and uniformity, was elaborated at the Rottweil powder-works, and appears to have been adopted into the German service for a time, but its first great promise of success seems to have failed of fulfilment through defects in stability.

Reference has already been made to the conversion of gun-cotton (trinitrocellulose), and to mixtures of it with less explosive forms of nitrated cotton (or cellulose of other description), by the action of solvents, into horn-like materials. These are in the first instance obtained in the form of gelatinous masses, which, prior to the complete evaporation, or removal in other ways, of the solvent, can be pressed or squirted into wires, rods, or tubes, or rolled or spread into sheets; when they have become hardened, they may be cut up into tablets, or into strips or pieces of size suitable for conversion into charges or cartridges. Numerous patents have been secured for the treatment of gun-cotton, nitro-cotton, or mixtures of these with other substances, by the methods indicated; but in this direction the German makers of the powder just now referred to seem to have secured priority. Experiments were made about a year and a half ago with powder produced in this way at Woolwich, and the Wetteren Powder Company, in Belgium, has also manufactured so-called paper powders, or horn-like preparations, of the same kind, which were brought forward as counterparts of the French small-arm and artillery smokeless powder.

Mr. Alfred Nobel, to whom the mining world is so largely indebted for the invention of dynamite and of other very efficient blasting agents, of which nitro-

glycerin is the basis, was the first to apply the latter explosive agent, in conjunction with one of the lower products of nitration of cellulose, to the production of a smokeless powder. This powder bears great resemblance to one of the most interesting of known violent explosive agents, also invented by Mr. Nobel, and called by him blasting gelatine, in consequence of its peculiar gelatinous character. When the nitro cotton is impregnated and allowed to digest with nitro-glycerin, it loses its fibrous nature and becomes gelatinised while assimilating the nitro-glycerin, the two substances furnishing a product which has almost the character of a compound. By macerating the nitro-cotton with from 7 to 10 per cent of nitro-glycerin, and maintaining the mixture warm, the whole soon becomes converted into a plastic material from which it is very difficult to separate a portion of either of its components. This preparation, and certain modifications of it, have acquired high importance as blasting agents more powerful than dynamite, and possessed of the valuable property that their prolonged immersion in water does not separate from them any appreciable proportion of nitro-glycerin.

In the earlier days of the attempted application of blasting gelatin to military uses, in Austria, when endeavours were there made to render the material less susceptible of accidental explosion on active service (as by the penetration of bullets or shell fragments into transport wagons containing supplies of the explosive), this result was achieved by Colonel Hess by incorporating with the components a small proportion of camphor, a substance which had then, for some time past, played an important part in the technical application of nitro-cotton to the production of the remarkable substitutes for ivory, horn, &c., known as Xylenite. By incorporating with nitro-glycerin a much larger proportion of nitro-cotton than used in the production of blasting gelatin, and by employing camphor as an agent for promoting the union of the two explosives, as well as, apparently, for deadening the violence or reducing the rapidity of explosion of the product, Mr. Nobel has obtained a material of almost horn-like character, which can be pressed into pellets or rolled into sheets while in the plastic condition, and which compares favourably with the gun-cotton preparations of somewhat similar physical characters just referred to, as regards ballistic properties, stability, and uniformity, besides being almost absolutely smokeless. The retention in its composition of some proportion of the volatile substance camphor, which may gradually be reduced in amount by evaporation, renders this explosive liable to undergo some modification in its ballistic properties in course of time; it is believed that this point has been dealt with by Mr. Nobel, and accounts from Italy speak favourably of the results of trials of his powder in small arms, while Mr. Krupp is reported to be carrying on experiments with it in guns of several calibres.

The Government Committee on Explosives, in endeavouring to render the above defect of Nobel's original powder, were led by their researches to the preparation of other varieties of nitro-glycerin powder, which when applied in the form of wires or rods, made up into sheaves or bundles, have given, in the service small-bore rifle, excellent ballistic results. The most promising of them, which fulfils, besides, the conditions of smokelessness and of stability, so far as can be guaranteed by the application of special tests of exposure to elevated temperatures, &c., is now being submitted to searching experiments with the view of so applying it in the arm as to overcome certain difficulties attending the employment, in a very small-bore rifle, of an explosive developing much greater energy than the black powder charge, which therefore gives very considerably higher velocities even with much smaller charges, and consequently heats the arm much more. Thus, the service black powder charge furnishes, with the small-bore rifle, an average (and variable) velocity of 1800 f.s., together with pressures ranging from

18 to 20 tons per square inch; on the other hand, with considerably less of the explosive referred to, there is no difficulty in securing a very uniform velocity of about 2200 f.s. with pressures not exceeding 17 tons, while velocities as high as 2500 f.s. are obtainable with pressures not greater than the maximum allowed with the black powder charge.

It is obvious, from what has already been said respecting the causes of the erosive action of powder in guns, that comparatively considerable erosive effects would be expected to be produced by powders of high energy as compared with black powder. Moreover, the freedom of the products of explosion from any solid substances, and consequently the absence of any fouling or deposition of residue in the arm, causes the heated surfaces of the projectile and of the interior of the barrel to remain clean, and in a condition, therefore, very favourable to close adherence together. If to these circumstances be added the fact that the behaviour of the smokeless powder has to be adapted to suit an arm, a cartridge, and a projectile originally designed for use with black powder, it will be understood that the devising of an explosive which shall be practically smokeless, sufficiently stable, and susceptible of perfectly safe use in the arm under all service conditions, easy of manufacture and not too costly, is, after all, but a small part of the difficult problem of adapting a smokeless powder successfully to the new military rifle—a problem which, however, appears to be on the near approach to satisfactory solution.

The experience already acquired in guns ranging in calibre from 1.85 inches to 6 inches, with the smokeless powder devised for use in our service, has been very promising, and indicates that the difficulties attending its adaptation to guns designed for black powder are likely to prove considerably less than in the case of the small-arm. But here again, the circumstance that much smaller charges are required to furnish the same ballistics as the service black powder charges, and that the comparatively gradual and sustained action of the new powder gives rise to lower pressures in the chamber of the gun, and higher pressures along the chase, demonstrate that the full utilisation of the ballistic advantages, and the increase in the power of guns of a given calibre and weight, with the new form of powder, are only attainable by some modifications in the designs of the guns—such as a reduction in size of the charge-chamber, and some additions to the strength, and perhaps, in some cases, of the length of the chase.

When, however, the smokeless powder has been adapted with success in all respects to artillery, from small machine guns to guns of comparatively heavy calibre, and when its ballistic advantages have been fully utilised in guns of suitable design, it will remain to be determined how far such a powder—undeniably of much more sensitive constitution than black powder, or any of its modifications—will withstand, unchanged and unharmed, the various vicissitudes of climate, and the service storage conditions in ships and on land in all parts of the world—a condition essential to its adaptability to naval and military use, and especially to the service of our Empire; and whether sufficient confidence can be placed in its stability for long periods under these extremely varied conditions to warrant the necessary freedom from apprehension of possible danger, emanating from within the material itself, to allow of its being substituted for black powder wherever its use may present advantages.

Possibly it might be that the storage, with perfect safety, of such a powder in ships, forts, or magazines, might demand the adoption of precautionary measures which might place some comparatively narrow limits upon the extent of its practicable service applications; even then, however, an imperative need for the introduction of special arrangements to secure safety and immunity from deterioration may be of small importance as compared with the great advantages which the provision of a

thoroughly efficient smokeless powder may secure to the possessor of it, especially in naval warfare.

That the opinions respecting the importance of such advantages are founded upon a sound basis one can hardly doubt, after the views expressed by several of the highest military and naval authorities, although opinions as to their extent may differ very considerably even among such authorities.

The accounts furnished from time to time from official and private sources of the effects observed at some considerable distance by witnesses of practice with the smokeless powders successively adopted in France, have doubtless been regarded by military authorities as warranting the belief that the employment of such powders must effect a great revolution in the conduct of campaigns. Not only have the absence of smoke and flame been dwelt upon as important factors in such a revolution, but the recorders of the achievements of smokeless powder—whose descriptions have doubtless been to some extent influenced by the vivid pictures already presented to them of what they *should* anticipate—have even been led to make such explicit assertions as to the *noiselessness* of these powders that high military authorities have actually been thereby misled to portray, by vivid word-painting, the contrast between the battles of the future and the past—to imagine the terrific din caused by the discharge of several hundred field-guns and the roar of musketry in the great battles of the past, giving place to noise so slight that distant troops will no longer receive indications where their comrades are engaged, while sentries and advanced posts will no longer be able to warn the main body of the approach of an enemy by the discharge of their rifles, and that battles might possibly be raging within a few miles of columns on the march without the fact becoming at once apparent to them.

It is somewhat difficult to conceive that in these comparatively enlightened days—an acquaintance with the first principles of physical science having for many years past constituted a preliminary condition of admission to the training establishments of the future warrior—the physical impossibility of such fairy tales as appear to be considered necessary in France for the delusion of the ordinary public, would not at once have been obvious. Yet even in professional publications in Germany, where we are led to expect that the judgment of experts would be comparatively unlikely to be led astray through lack of scientific knowledge, we have, during the earlier part of last year, read in articles upon the influence of smokeless powder upon the art of war (based evidently upon the reports received from France) such passages as these:—"The art of war gains in no way as far as simplicity is concerned; on the contrary, it appears to us that the absence of so important a mechanical means of help as *noise* and smoke were to the commander, requires increased skill and circumspection in addition to the qualities demanded by a general. . . ." "The course of a fight will certainly be mysterious on account of the *relative stillness* with which it will be carried on."

In an amusing article, in imitation of the account of the Battle of Dorking, which appeared in the *Deutsche Heeres Zeitung* of April last, the consternation is described with which a battalion receives the information from a wounded fugitive from the outposts that the enemy's bullets have been playing havoc among them, without any visible or audible indications as to the quarter of attack. Later in the year, and especially since the manoeuvres before the German and Austrian Emperors, when the employment of the new smokeless powder was the event of the day, the absurdity of the assertions as to the noiselessness of the new powders became a theme for strong observations in the German service papers; the assumed existence of a noiseless powder was ridiculed as a thing equally impossible with a recoilless powder; the violence of the report, or explosion, produced upon the discharge of a firearm being in direct relation to the

volume and tension of the gaseous matter projected into the surrounding air.

The circumstance that blank ammunition was alone used in the smokeless powder exhibition at the German manoeuvres may have served to lend some support to the assertions as to *comparatively* little noise made by the powder—the report of blank cartridges being slight on account of the small and lightly confined charges used. It is said that the sound of practice with blank ammunition at the German manoeuvres was scarcely recognised at a distance of 100 metres. In a recently published pamphlet on the results of employment of the latest German smokeless powder in the manoeuvres, it is stated, on the other hand, that the difference between the violence of the report of the new powder and of black powder is scarcely perceptible; that it is sharper and more ringing, but not of such long duration. This description accords exactly with our own experience of the reports produced by different varieties of smokeless powder, and of the lecturer's earlier experience with gun-cotton charges fired from rifles and field guns. The noise produced by the latter was decidedly more ringing and distressing to the ear in close proximity to the gun, but also of decidedly less volume, than the report of a black-powder charge when heard at a considerable distance from the gun.

As regards smokelessness, the present German service powder is not actually smokeless, but produces a thin, almost transparent, bluish cloud which is immediately dissipated. Independent rifle-firing was not rendered visible by the smoke produced at a distance of 300 metres, and at shorter ranges the smoke presented the appearance of a puff from a cigar. The most rapid salvo-firing during the operations near Spandau did not have the effect of obscuring those firing from distant observers.

That in future warfare, if smokeless, or nearly smokeless, powders have maintained their position as safe and reliable propelling agents for small arms and field artillery, belligerents of both sides will be alike users of them, there can be no doubt. The consequent absence of the screening effect of smoke—which, on the one hand, removes an important protection and the means of making rapid advances or sudden changes of position in comparative safety, and, on the other hand, secures to both sides the power of ensuring to the fullest extent accuracy of shooting, and of making deadly attack by individual fire through the medium of cover with comparative immunity from detection—can scarcely fail to change more or less radically many of the existing conditions under which engagements are fought.

As regards the naval service, it is especially and, at present at any rate, exclusively for the new machine and quick-firing guns that a smokeless powder is wanted; for such service the advantages which would be secured by the provision of a reliable powder of this kind can scarcely be over-estimated, and their realisation within no distant period may, it is believed, be anticipated with confidence.

The Chemical Laboratory of Wiesbaden.—In the Winter Term 1889-90 there were 62 students on the books. Of these 46 were from Germany, 3 from England, 2 from Austro-Hungary, 2 from France, 2 from Spain, 1 from Russia, 2 from North America, 1 from Holland, 1 from Norway, 1 from Chili. Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, and Architect J. Brahm. The assistants in the instruction laboratory are two in number, in the private laboratory 16, and in the Versuchsstation 3. The next Summer Term begins on the 24th of April. Besides the scientific researches, a great number of analyses were undertaken in the different Departments of the Laboratory, and in the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

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Professor of Chemistry in the University of Virginia.

(Continued from p. 140).

Seventh Series of Experiments.

IN pursuance of the attempt to connect directly the atomic weight of gold with that of hydrogen, metallic zinc was prepared as nearly as possible in a state of purity, and, a known quantity of the metal having been dissolved in dilute sulphuric acid, the amount of hydrogen evolved was determined by volume. A solution of pure auric chloride or bromide was then treated with a known quantity of the same zinc, more than sufficient for the complete precipitation of all the gold present; the excess of zinc was dissolved by dilute sulphuric acid, and the volume of hydrogen given off was determined. The precipitated gold was carefully collected, washed, dried, ignited, and weighed. The difference between the volume of hydrogen which the zinc gave when thus partly used to replace a known quantity of gold and the volume which it would have given if replacing hydrogen alone, represented, of course, the volume of a quantity of hydrogen equivalent to the gold precipitated and weighed. From this volume, under known conditions of temperature and pressure, the weight of the hydrogen was calculated on the basis of Regnault's results for the density of the gas, after application of the needful corrections, as in the sixth series of these experiments.

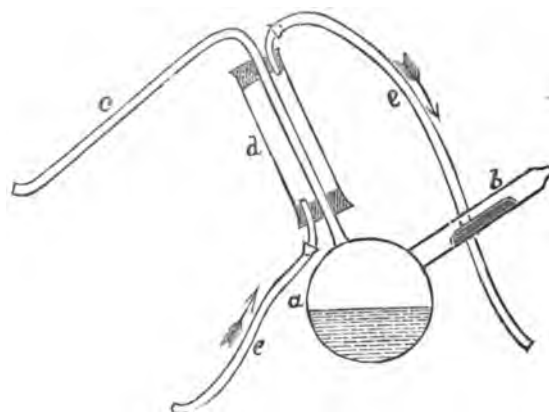
In a preliminary notice of my work read before the Chemical Section of the British Association at the Manchester meeting of 1887, it was pointed out that the method just described has certain advantages in principle. It does not require that the weight of the gold salt in solution be known, so that all difficulties in regard to drying such salt without decomposition are disposed of. It does not depend upon a knowledge of the atomic weight of the halogen in combination with gold, or upon a knowledge of the atomic weight of zinc. It does not even require that the zinc be of assured purity, provided only it be uniform in character, so that a given weight of it can be trusted to yield always the same quantity of hydrogen, and there be no impurities present capable of interfering with the collection of the whole of the precipitated metallic gold in a state of purity. The chief difficulty consists in the accurate ascertainment of the total volume of hydrogen evolved from the solution of a satisfactorily large quantity of zinc; when the gold solution comes to be used, as the volume of hydrogen given off on solution of the surplus zinc may be made quite small, its measurement becomes both easy and exact.

The pure zinc required was obtained by fractionally distilling in a Sprengel vacuum some very nearly pure metal from the Bertha Zinc Works, in South-Western Virginia, using a long combustion-tube of hard Bohemian glass, and substantially the same arrangement of apparatus as that described by Morse and Burton† in connection with their work on the atomic weight of zinc. The original metal was found, by an analysis in the laboratory of the University of Virginia, to contain less than 0.04 per cent of foreign matter, almost solely consisting of lead and iron. It was four or five times re-distilled *in vacuo*, rejecting each time about one-third of the quantity treated. The process is easily carried out, and in the final product, completely soluble in dilute sulphuric acid without visible residue, no trace of detectable impurity could be found.

For the evolution of hydrogen on solution of this zinc

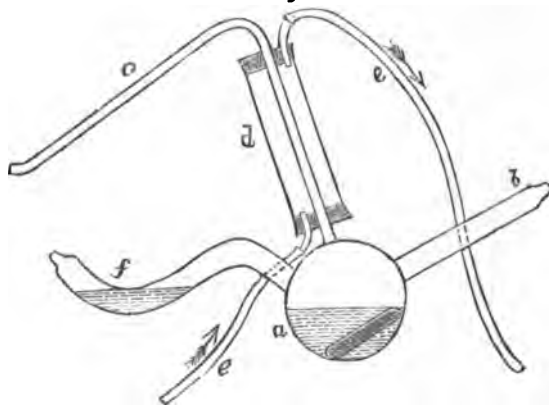
in acid the little piece of apparatus represented in Fig. 8 was used, the same that I had used in my work of several years ago on the atomic weight of aluminum.* The description formerly given of the details of an experiment with this apparatus may be repeated with but trifling change of language. A rather more than sufficient quantity of diluted sulphuric acid, its volume accurately measured, having been introduced into the bulb *a* by means of a little tube-funnel passed through the tube *b*,

FIG. 8.



the outer end of which was originally open, taking care to leave the surface of *b* clean, the metallic zinc, in a single piece of elongated shape, and having a little piece of slender platinum wire wrapped round it, was passed into *b*, held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 m.m. from it; *b* was now drawn off in the lamp flame, and sealed with a well-rounded end. The bulb was touched for a moment or two with the hand, so as to expel a very little air, and the outer end of the small tube *c* was introduced into the mercury of the trough, taking care that *b* was

FIG. 9.



still kept in such a position as to prevent the zinc coming in contact with the dilute acid. After a sufficient lapse of time for the apparatus to have acquired the temperature of the room, the barometer and thermometer and the difference of level of the mercury in the trough and in *c* were read off;† so that, knowing the volume of dilute acid introduced and of metallic zinc (the latter from its weight), calibration of the bulb and tubes after the experiment was over completed the data necessary to

* A Paper read before the Royal Society, May 9, 1889.

† *American Chemical Journal*, vol. x., p. 312. Tubes of glazed porcelain, closed at one end, had been specially procured for use in thus distilling zinc, but it was found that they were quite unnecessary.

* *Phil. Trans.*, 1880, p. 1026.

† All readings were, of course, made from a distance with the aid of a small telescope.

determine the volume of air which the apparatus contained at the beginning. The piece of zinc was now made to slide down into the bulb, the end of the gas delivery-tube *c* having been brought under the mouth of the measuring flask. Over-rapid evolution of hydrogen and any considerable rise of temperature were prevented, partly by tilting the bulb so that the little piece of zinc rested against one side and exposed but a part of its surface to the action of the liquid, and partly by cooling the outside of the bulb with water. To guard against more than traces of aqueous vapour being carried away with the hydrogen, a rapid current of ice-water was kept up through *d*.

As soon as the last of the zinc had disappeared, leaving the liquid quite clear, *c* was brought up into a nearly vertical position, and the apparatus left to itself until the temperature of the room had been attained. The barometer and thermometer and the height of the mercury in *c* above that in the trough were now read and recorded.

Lifting *c* straight up from the trough, the mercury in this tube was got out by running a wire up and down in it, and inverting it, the whole of the remaining space in *a*, *b*, and *c* was filled up with solution of zinc sulphate and free acid of the same strength with that already contained, this liquid being run in from a graduated burette through a slender tube-funnel, and the volume used noted, so as to show how much liquid had been already present.

The apparatus having been now emptied, washed out, and calibrated (with water, instead of mercury, on account of the difficulty of getting the interior quite dry), the volume of gas remaining in it at the close of the experiment was had from the difference between the total capacity (to the level of the mercury in *c*) and the volume of liquid which the bulb had contained at the close of the experiment, these taken together with the data for pressure and temperature.

The dilute acid was saturated with pure hydrogen just before being used (and in the experiments with auric chloride or bromide the main portion of water holding this salt in solution was similarly treated), and a preliminary experiment showed that there was but an extremely minute difference between the amount of gas removable from such liquid by heating in a Sprengel vacuum and from that containing zinc sulphate after the solution of the metal; so that, practically, the question of retention of gas in solution by the liquid might be neglected.

The sulphuric acid was diluted to 25 per cent by weight, only a small bit of platinum wire was wrapped round the zinc, and the temperature of the bulb was not allowed to rise beyond about 20° C. Thus the risk of evolving other gaseous products than hydrogen*—as hydrogen sulphide or sulphur dioxide—was avoided, and on testing for these impurities the hydrogen collected no traces of them were found.

The measuring-flask used to collect the hydrogen was of the same character as that used for the experiments of the sixth series, but of much larger size, holding about a litre. The quantity of zinc taken for each experiment was calculated to give a volume of gas which, under the conditions of temperature and pressure of the day, would bring the mercury to somewhere near the middle of the neck, and the gas, previously dried by balls of fused potash, was measured after the temperature had been rendered as nearly as possible fixed by the circulation round the outside of the flask of an active stream of water from the laboratory supply pipes. On account of slight rise of temperature during the solution of the metal, the volume of hydrogen left in the bulb and tubes was always less than that of the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the gas collected in the flask.

* Muir and Adie: "On the Interaction of Zinc and Sulphuric Acid," *Chem. Soc. Journ.*, Jan., 1888, p. 47.

In the experiments with auric chloride or bromide the quantity of hydrogen given off on solution of the *surplus* zinc was so small that it could be easily measured in a little gas tube, the same method of double calibration with mercury being used as for the larger volumes. In these experiments the bulb used had a second side tube, *f*, as shown in Fig. 9, to hold the sulphuric acid, while *a* contained the aqueous solution of the gold salt; this acid was already somewhat diluted, and was introduced into *a*, after complete precipitation of the gold, very gradually, so as to avoid any considerable rise of temperature. The quantity of water used was such as to make the whole volume of liquid very nearly the same in the experiments with zinc alone and in those with zinc and the auric salt. Care was taken to ascertain, after measurement of the hydrogen, that it had been effectually freed by the potash balls not only from moisture, but from any traces of hydrochloric acid formed and carried over.

In order to connect the weight of the zinc with that of the hydrogen produced by its solution, it was necessary that the weight of the metal should be *absolute*, or in terms of equal value with those used in Regnault's researches on the density of hydrogen; hence, as has been already stated, the weights used were such as had had their real values determined, and the precaution of double weighing was applied. The quantities of metal used being small, the centre of gravity of the balance beam was so adjusted as to give great sensitiveness. In calculating the weight of the hydrogen from its volume, the same value for the weight of a litre of the gas was assumed, as has been already stated, viz., 0.08979 grm., being the result of Regnault's determinations, with the correction pointed out by Lord Rayleigh and numerically estimated by Crafts, and further corrected for the force of gravity at the University of Virginia.

The haloid salts of gold were prepared as for the experiments of the first and second series, and the careful filtration of their solutions was followed by long-continued standing at rest before the portions required were gently drawn off for use. Great care was taken in removing the last traces of precipitated gold from the bulb—to facilitate which the connected tubes were all cut off short—and in repeatedly washing the metal, first with dilute sulphuric acid, then with pure hydrochloric acid, and finally with water, before drying, heating (in the Sprengel vacuum), cooling, and weighing.

The results obtained by this method were much more free from irregularity, and much more satisfactory, than those of the electrolytic experiments. All are reported, except one or two cases obviously vitiated by mechanical defects of manipulation, and in consequence, not carried out to the end.

Experiments with Zinc alone.

Exper.	Zinc dissolved. Grm.	Hydrogen obtained at 0° C. and 760 m. m. C. c.	Hydrogen at 0° C. and 760 m. m. for 1 grm. of zinc. C. c.
I.	2.6990	922.64	341.85
II.	2.6771	915.33	341.91
III.	2.7029	924.20	341.93
IV.	2.7117	927.51	342.04

Equivalent
to

Or a total amount of 10.7907 grm. of zinc gave 3689.68 c.c. of gas,* equivalent to 341.93 c.c. of hydrogen for 1

* These figures represent an atomic weight for zinc = 65.124, taking the weight of a litre of hydrogen at 0° C. and 760 m. m. as 0.08979 grm., and assuming the zinc used to have been absolutely pure, and the quantity of hydrogen collected to have been strictly equivalent to it; neither of the two latter assumptions is essential to the use made in this paper of the experiments. Reynolds and Ramsay, in their recent paper (*Chem. Soc. Journ.*, Dec., 1887, p. 854) on the atomic weight of zinc, arrive at a somewhat higher value on the basis of a like comparison of the weight of the metal with the volume of hydrogen liberated by it, but they assume the weight of the litre of hydrogen under normal temperature and pressure as 0.0896 grm., which must be considered too low in view of the recently applied correction of Lord Rayleigh.

Experiments with Gold Salt and Zinc.

Exper.	Character of gold used.	Character of gold salt.	Gold precipitated. Grm.	Hydrogen at 0° C. and 760 m.m.		Hydrogen equivalent to gold.	
				Corresponding to total zinc. C.c.	Obtained from residual zinc. C.c.	Vol. at 0° C. and 760 m.m. C.c.	Weight. Grm.
I.	A, b	AuCl ₃	10.3512	1779.44	-23.34	= 1756.10	= 0.15768
II.	A, b	AuBr ₃	8.2525	1428.99	-28.61	= 1400.38	= 0.12574
III.	A, b	AuCl ₃	8.1004	1393.43	-18.56	= 1374.87	= 0.12345
IV.	C	AuCl ₃	3.2913	582.82	-24.18	= 558.64	= 0.05016
V.	C	AuBr ₃	3.4835	606.20	-15.27	= 590.93	= 0.05306
VI.	D	AuBr ₃	3.6421	643.31	-25.20	= 619.11	= 0.05550

gm. of zinc. This value was adopted in calculating the fifth column of the above Table.

In considering possible causes of constant error in the experiments of this last series, it seems most likely that they would affect the exact determination of the weight of the precipitated gold, either by mechanical loss of some minute particles of the metal, tending to lower the atomic weight, or by incomplete washing out of the zinc salt, with an influence in the opposite direction. Any failure to remove the last traces of moisture from the hydrogen was, I think, effectually guarded against, at any rate within such limits as would have sensibly affected the resulting atomic weight; and any error due to retention of hydrogen in solution by the liquid must also have been inappreciably small, in view of the precautions taken and the close similarity of conditions in the experiments with zinc alone and with zinc and the auric salt.

(To be continued).

SOME LECTURE EXPERIMENTS.

By A. A. BRENNEMAN.

1. *The Dissociation of Soap by Water.*—A well-filtered alcoholic solution of soap containing a little phenolphthalein is poured carefully into a glass cylinder half filled with distilled water, which also contains phenolphthalein. The line of contact of the liquid is coloured bright red, and, on carefully stirring with a long rod, a pink flush is diffused through the mixed liquids. As both are free from colour before contact, the liberation of alkali by the water is plainly shown, and the theory of the action of soap is thus illustrated. The alcohol may be of fifty to eighty per cent, and should contain a large quantity of soap in solution. The cylinder is tilted at forty-five degrees in pouring in the soap solution so that the layers of liquid may be distinct.

2. *Dissociation of Ammonium Chloride by Heat.*—The following experiment is easily performed and requires much less apparatus than such as require the separation of the dissociated constituents by diffusion through a porous cylinder. It depends simply upon the greater solubility of ammonia gas in water as compared with gaseous hydrochloric acid.

Into a long-necked, round-bottomed Bohemian flask is put three to five grms. solid NH₄Cl, and the flask is heated over a gas lamp (best a triple burner) until the solid has nearly disappeared and the bulb of the flask is filled with transparent gas. A glass rod having a strip of moistened red litmus-paper wound spirally around it for four inches of its length is then introduced as far as the bulb. On withdrawing it after ten seconds the paper will be entirely blue, and, if still moist, will then turn red on quickly exposing it to the fumes issuing from the mouth of the flask.

After cooling, the residual NH₄Cl may be dissolved in water and tested with litmus to show its faintly acid reaction. Ordinary sublimed NH₄Cl is faintly acid, but a sample purified by solution and re-crystallisation will be so nearly neutral that the greater acidity of the sample from the flask will be quite apparent. If, during the

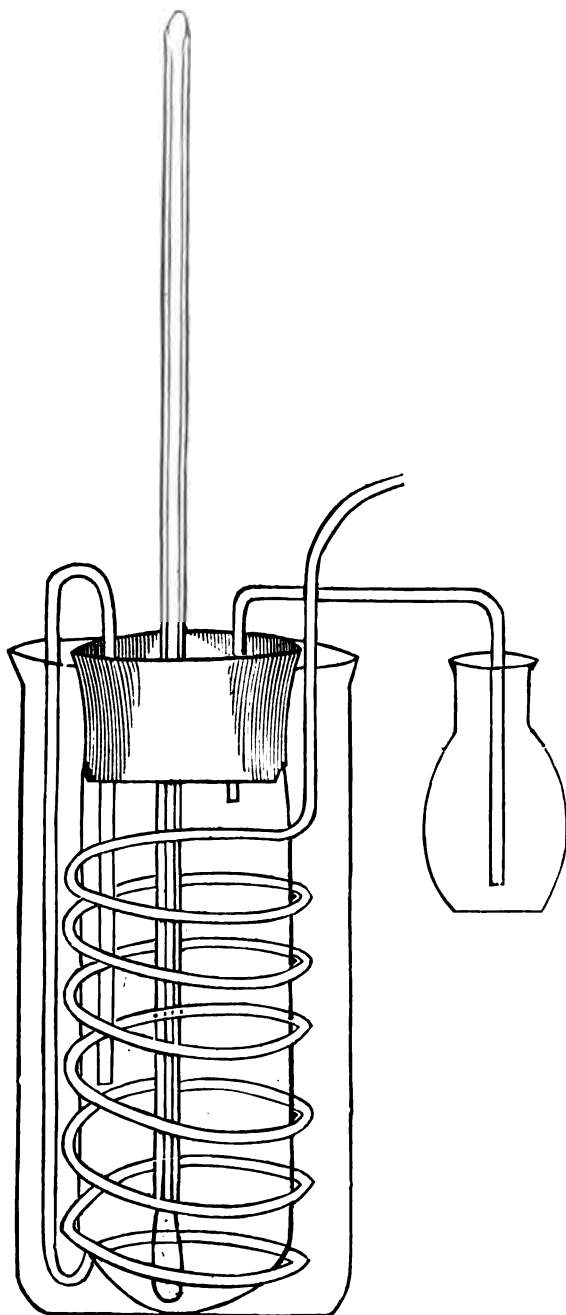
heating of the flask, a thick dry rod, previously cooled by ice or ether, be inserted into the transparent gases of the heated flask, heavy clouds of NHCl are produced.

3. *Opaque Soap Bubbles for many Forms of Gas Experiment.*—Two flasks, arranged like gas-washing bottles and tied together so as to be handled as one, are filled to the depth of 1.5 c.c. with strong NH₃ and HNO₃ respectively. The long tube of each bottle reaches to within one c.m. of the surface of the liquid, but does not touch it; the short tube ends just below the stopper in each bottle. On forcing any gas first through the long tube into the bottle containing HNO₃, and from that through the connecting tube against the surface of the NH₃ solution in the other flask, dense white fumes of NH₄NO₃ are produced and bubbles may be blown with the gas from the second bottle. Nitric acid is preferable to HCl, as fumes of NH₄Cl soon choke the exit tube, while NH₄NO₃ is deliquescent in presence of moist NH₃ gas. Also, the gas must pass last through the NH₃ bottle, as otherwise nitric acid fumes will be in excess in the mixture and the soap will be decomposed, preventing formation of bubbles. Such bubbles are more readily visible by daylight or gas-light, and much more satisfactory for use before large audiences. The quantity of vapour added is too trifling to affect the density of the gas, and the properties of weight, combustibility, &c., may be illustrated as usual. With CO₂, however, the rapid formation of ammonium carbonate in the second bottle necessitates a little practice in manipulating the apparatus.—*Journal of the American Chemical Society*, Vol. xii., No. 2.

THE IGNITING-POINT OF SULPHUR.

By BERTRAM BLOUNT.

AFTER writing my last letter on this subject, which appeared in the *CHEMICAL NEWS*, vol. lxi., p. 108, my attention was called to a paper by Mr. J. Rutherford Hill in the *Pharmaceutical Journal* of March 1st, in which he detailed the method of experiment he had used, and gave as his result a temperature of 248° C. This differed so widely from my own experience that I proceeded, as soon as opportunity presented, to repeat the determination by the method he had adopted. The apparatus employed by Mr. Rutherford Hill is figured in the *CHEMICAL NEWS*, vol. lxi., p. 125, and it was there that I first saw it, while that which I fitted up was based on his written description in the *Pharmaceutical Journal*. The accompanying figure shows the arrangement. The sulphur is contained in a test-tube immersed in a beaker of sulphuric acid. The test-tube is provided with a three-holed cork, through which pass a thermometer whose bulb dips into the sulphur, a glass tube extending downwards nearly to the surface of the sulphur, and another glass tube terminating at the under side of the cork. The free end of the former of these tubes is wound spirally round the test-tube, and is finally connected with a water-pump (not shown), supplying a blast of air, the arrow indicating the entrance of the steam. The latter (the exit tube) leads into a small flask containing a little water. In performing the experiment the temperature of



the sulphur is gradually raised by heating the sulphuric acid bath, and the stream of air is regulated by a screw-clip until about three bubbles per second pass, the rate being shown by the end of the exit tube dipping into water in the small flask. The air-supply is heated by passing through the spiral of glass tubing coiled round the test-tube, and the stream of air being kept fairly small, cooling of the sulphur or sulphur vapour is avoided.

Using this apparatus, I found that the air took fire in sulphur vapour at 266°C ., burning with a blue flame at the mouth of the ingoing tube, and, on allowing the temperature to fall, ceased to ignite at 261°C . These tem-

peratures are not far removed from those obtained by Mr. Rutherford Hill, and the difference between his and my results probably lies in the different temperature of the air current, and perhaps in the actual dimensions and arrangement of the apparatus and the area of the surfaces of glass in contact with the mixed gases. I do not think that my higher figures are due to any heating of the thermometer by the flame, as the bulb of the instrument was protected from it by immersion in the fused sulphur, and, moreover, no sudden rise was observed at the point of ignition.

It is plain from this that my former statement of what I believed to be the igniting-point of sulphur is erroneous, there being no doubt as to the superiority of this plan over that I formerly used. In the light of more recent experience I am inclined to regard the higher result then obtained as due to the exclusion of the air from the capsule containing the sulphur by sulphur vapour, thus hindering ignition.

In conclusion I must thank Mr. Rutherford Hill for the very excellent and accurate method he has devised, and the satisfactory termination to which he has brought this question.

Laboratory, Broadway,
Westminster, S.W.
March 15, 1890.

DETERMINATION OF POTASSA AND HUMUS IN SOILS.

By J. RAULIN.

THE author's process depends on the very slight solubility of potassium phosphomolybdate in aqueous liquids, whilst the corresponding sodium, magnesium, calcium, iron, and aluminium salts are more or less soluble. A relatively small sample of the soil may be taken for analysis, since the phosphomolybdate weighed is nineteen times as heavy as the potassa to be determined.

A solution of phosphomolybdic acid is prepared by dissolving 100 grms. pure crystalline ammonium molybdate in a minimum of water, and adding 6.5 grms. neutral crystalline ammonium phosphate dissolved in a little water. Aqua regia is added when ammonium phosphomolybdate is thrown down. It is then heated, adding aqua regia from time to time, until the precipitate is redissolved. It is evaporated to dryness, first over the naked flame, and then in the water-bath at about 70° . The author adds 400 c.c. of water, 5 c.c. of nitric acid, heats, and filters, when the phosphomolybdic reagent is ready.

A liquid for washing the potassium phosphomolybdate is obtained by dissolving 20 grms. sodium nitrate in 1 litre of water, 2 c.c. of pure nitric acid, and 1.2 c.c. of a solution of nitre, at 80 grms. per litre, slightly heated, to saturate the liquid with potassium phosphomolybdate. It is stirred up, let settle, and the clear liquid is decanted.

To prepare the solution in which the potassa is to be determined, a portion of the soil in question, containing about 15 m.grms. of anhydrous potassa, is accurately weighed off. The potassium salts are extracted by the usual means, they are separated from the larger part of the calcareous, ferruginous, and aluminous salts, and converted into nitrates. The liquid is concentrated down to a few c.c., and slightly acidulated with nitric acid. The author then adds 4 c.c. of the phosphomolybdic reagent for every 10 m.grms. of anhydrous potassa supposed to be present. It is evaporated to dryness at 50° , and then filtered through very small counterpoised double filters, each double, washing the precipitate with the solution mentioned above. The counterpoise is washed with the same liquid, and the filters are dried at 50° and weighed. The weight multiplied by $\frac{52}{100}$ gives the potassium oxide,

A volumetric determination of humus in soils by a solution of permanganate would be practical if the combustion of the organic matter were complete, and if the end of the reaction were not masked by the brown colour.

The author modifies the process of J. H. Schmidt as follows:—

In a small flat-bottomed flask, holding one-fourth litre, he introduces 10 c.c. of a solution of manganese sulphate (16 grms. of the anhydrous salt per litre), and 10 c.c. of a solution of permanganate, at 10 grms. per litre, and heats for a few moments, when the liquid is decolourised and "manganese bronze" is precipitated. He adds 100 c.c. water, and 4 c.c. of sulphuric acid (150 c.c. of the monohydrated acid per litre). He further adds an exactly measured volume of a humic liquid suitably prepared, so that when becoming completely oxidised it may destroy at most half the manganese peroxide. The mixture is gently boiled for eight hours, renewing the water as it is driven off.

The manganese peroxide not attacked is dissolved in heat in a small measured excess of decinormal oxalic acid, and the excess of the latter is destroyed by a solution of permanganate at 1 gram. per litre, which is dropped in until a slight rose tint appears.

The volume of oxalic acid not destroyed is calculated from the volume of permanganate dropped in, the correspondence of the two liquids having been found by a previous trial. The volume of oxalic acid which destroys the same quantity of peroxide which the humus introduces is calculated by taking the difference between the volume of oxalic acid required to destroy all the peroxide formed by 10 c.c. of permanganate at 10 grms. per litre, and the volume of oxalic acid which has destroyed the peroxide remaining after the action of the humus. The former volume of oxalic acid, *i.e.*, that which has destroyed the peroxide formed by 10 c.c. of permanganate, has been determined by a previous trial.

As for the humic liquor, it is prepared from 10 grms. of soil treated with soda in the usual manner. It will be easy to calculate the volume of oxalic acid equivalent to the total volume of the humic liquid, of which a known fraction has been tried, and consequently the volume of oxalic liquid equivalent to the humus of 10 grms. of dry soil.

This number of c.c. of the oxalic liquid multiplied by 0.8 m.grm. will express in m.grms. the weight of oxygen necessary to burn the humus of 10 grms. of dry soil.—*Comptes Rendus*, cx., p. 289.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

March 21, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

Mr. A. E. CHILDS was elected a member of the Society.

The following communications were read:—

"*The Villari Critical Point in Nickel and Iron.*" By HERBERT TOMLINSON, F.R.S.

Villari has shown that the permeability of iron is increased by longitudinal traction, provided the magnetising force does not exceed a certain limit, but beyond this limit traction produces a decrease of permeability. The value of the force for which traction produces no change in the permeability is known as the Villari critical point.

As far as the author is aware, no previous observer has found a similar critical point for nickel, but by confining his attention to temporary magnetisation, he has detected such a point with comparative ease. He has also examined the variation of the Villari critical points in iron and nickel with change of load, and has investigated the

influence of permanent strain on these points. The experiments were made by the ballistic method, using wires about 400 diameters long. In each set of observations the permeability was obtained with various loads, the magnetising force being kept the same, and with each load the circuit was closed and opened until the swings on make and break were equal; this swing was taken as a measure of the induction under the given load.

Several diagrams accompany the paper, in which load and percentage change of permeability are plotted, regard being had to sign.

The author finds that for annealed unstrained iron the critical value of the force decreases as the load increases, and that the Villari point is much lower for temporary than for total magnetisation. With a load of 4.7 kilos. on a 1 m.m. wire, the value of the force giving the temporary point was 2.8 C.G.S. units. He also found that for a given magnetising force there were generally two loads, which have no effect on the temporary magnetisation.

With unstrained nickel the critical value of the force is much greater than in iron, being about 114 C.G.S. units for a load of 10 kilos. on a wire 0.8 m.m. diameter, and 67 for a load of 6.6 kilos.; for a force of 21 units no critical point exists.

Experiments on a permanently strained iron wire show that for magnetising forces ranging from 0.03 to 0.3 there is no critical point, and all the resulting curves are identical. There is, however, considerable difference in the observations taken during loading and those taken on unloading. For greater magnetising forces the curves cease to be identical, and the maximum increase of permeability becomes less and less, until for a certain force the curves begin to cut the load line. As the force increases beyond this value the point of cutting approaches the zero, and the curves begin to cut the load line in two points. Further increase of force to 3 C.G.S. units causes the first point to disappear and the second point recedes from the origin. Finally, with sufficiently high magnetising forces, the second point cannot be reached before the wire breaks, and the curve lies entirely below the load line.

With nickel the curves for very minute forces, like those of iron, are exactly the same for λ , different values of the force, but they lie below the load line, *i.e.*, the permeability is diminished by loading; there is no difference, however, in the loading and unloading curves. Beyond a certain value of the force, the identity of the curves ceases, and that part of the curve near the origin bulges towards the load line. For a force a little over 21 C.G.S. units the permeability begins to increase with load, and the curve cuts the line in one point, which point recedes from the origin as the force increases.

Mr. SHELFORD BIDWELL said that Prof. J. J. Thomson, reasoning from the change of length by magnetisation, had predicted a Villari point in cobalt when compressed, and this was verified experimentally. On applying similar reasoning to nickel, he (the speaker) did not expect to find a Villari point, and both Sir W. Thomson and Prof. Ewing had searched in vain for one. In some experiments, not yet completed, he had examined the behaviour of nickel, both loaded and unloaded, when subjected to various magnetising forces. These show that the metal always contracts when magnetised. For no load the contraction at first increases with the magnetising force, but attains a maximum. With a moderate load the contraction is less for small forces, but for larger forces becomes equal, and then exceeds the contraction of the unloaded wire. For greater loads the contraction is less than when unloaded for all values of the force.

"*On Bertrand's Idiocyphalous Prism.*" By Prof. S. P. THOMPSON, D.Sc.

This hitherto undescribed prism is a total reflection one, made of calc spar, which shows to the unaided eye the rings and crosses such as are seen when a slice of

spar is examined by convergent light in a polariscope. The space is cut so that the light after the first reflection passes along the optic axis, and after the second reflection emerges parallel to the incident light. The rings and brushes are present in pairs, but two pairs may be seen by tilting the prism to one side or the other. This was demonstrated before the Society.

Prof. Thompson also exhibited a similar prism cut from quartz. Owing to the feeble double-refracting of the substance no conspicuous rings could be seen, but when examined by the lantern traces of such rings were visible.

"On the Shape of Movable Coils used in Electrical Measuring Instruments." By T. MATHER.

The object of this note is to determine the best shape of the horizontal section of swinging coils, such as are used in D'Arsonval galvanometers, electro-dynamometers, Wattmeters, &c. Assuming constant period and constant moment of inertia about the axis of rotation, it is shown that for zero instruments the best shape of the section is two circles, tangential to the direction of the deflecting field at the point about which the coil turns. A table accompanies the paper, in which various forms of section are given together with their relative deflecting moments per unit moment of inertia; the coils being taken of equal lengths, and the current density being constant. From this table it appears that ordinary D'Arsonval coils only give about 45 per cent of the maximum deflecting moment, and ordinary Siemens dynamometers from 40 to 53 per cent.

The various assumptions made in the paper are shown to be justifiable in commercial instruments, and the modifications necessary in special cases are pointed out.

Mr. C. V. BOYS said he had when working at his radio-micrometer arrived at a shape similar to that recommended in the paper. He also noticed a peculiar relation true for all shapes where the length parallel to the axis of rotation is great compared with the breadth. Suppose a coil of any dimensions, then another coil of half the breadth and double the length and cross section will be dynamically, electrically, and magnetically the same as the original; for the moment of inertia, the electric resistance and the enclosed magnetic field are equal. The above relation is also true where the breadth is not small if the cross-pieces be thickened near the axis, so as to make their moment of inertia proportional to their length. He enquired whether the author had considered the subject of grading the movable coils; he himself was of opinion that, unlike fixed galvanometer coils, the wire near the axis should be thicker than that further away.

The PRESIDENT remarked that, in 1881, Prof. Perry and himself exhibited a Wattmeter at the Society of Arts whose movable coil somewhat resembled one of those in the paper, which gave a deflecting moment of 95 per cent of the maximum. In designing the instrument they had felt that the ordinary method of using a comparatively large swinging coil was not the best, and this led them to the shape adopted.

Our author regards electricity as "a mode of motion, a flow of molecular vibrations produced by the friction of molecules against molecules, which, by various methods, have been brought into different conditions and conveyed away by the best conductor." This theory he endeavours to prove by means of thermo-electricity.

His thermo-couples are made of soft iron and of an alloy of zinc and antimony. In forming these couples great care seems to have been taken, and the majority of the experiments have been repeated more than a dozen times.

We cannot describe Mr. Rust's interesting experiments without reproducing the numerous cuts with which they are illustrated. He concludes, as the law of thermo-electricity, that the electromotive force is proportional to the rate of speed at which heat passes the two junctions. He holds that there are not two electricities, but one; further, that there is "only one material force, viz., heat; and that electricity and light proceed from it." He considers that the results of the electrical experiments in high vacua made by Mr. Crookes are precisely what might have been expected, whilst, in an absolute vacuum, no electric current could pass.

His thermo-electric furnace of 6000 elements generated such a heat that the lower iron parts melted like wax. With various improvements, some of them suggested by Prof. Silvanus P. Thompson, he hopes that this "magnopile" will become a commercial success.

Synoptical Tables of Inorganic and Organic Chemistry.

Compiled by CLEMENT J. LEAPER, F.C.S. London: G. Gill and Sons.

THIS work is avowedly examinational, being "adapted to the requirements of students preparing for the South Kensington Examinations." On this point we do not need to repeat the opinion which we have so often been compelled to express. But we feel bound to signalise the ingenuity of those authors who still contrive to present the familiar facts of elementary chemistry in some new form.

The tables, we find, are to be committed to memory.

In the glossary of chemical terms a non-metal is defined as "a substance yielding an oxide which, by admixture with water, produces an acid." Hence, accordingly, chromium, manganese, molybdenum, tungsten, &c., must in future rank as non-metals.

Amongst the laws, that of the conservation of energy is omitted.

Nitric anhydride is said to be a "whole crystalline solid," an expression not sufficiently clear.

Passing over not a few questionable statements, we find the formic, acetic, oxalic, tartaric, and salicylic acids enumerated as "the commoner organic acids." Mr. Leaper must be aware that, e.g., the citric and malic acids are far commoner, as well as more important, than the salicylic. It may, perhaps, seem hypercritical in us to point out such trifling errors. But in tables which are to be committed to memory "as a solid groundwork for future reading and research," no inaccuracy should, we submit, be suffered to exist.

NOTICES OF BOOKS.

Electricity: Theoretically and Practically Considered.

By ARTHUR RUST. London: E. and F. N. Spon.

WHAT is electricity? So far is this question yet from being answered that there still exists a heretic in Science—there are such persons!—who maintains that electricity is a form of matter, one of the components of water which escapes on freezing. This escape or decomposition the individual in question proclaims to be the reason why ice is specifically lighter than water! Hence Mr. Rust, in his special study of thermo-electricity, has done good work. Here, surely, we have a means of generating or liberating electricity in which water cannot be supposed to play a part.

Detection of the Elements of the Tissues of Wheat and Rye Meal.—P. Soltsien (*Pharm. Zeitung*).—The sample is comminuted, and a large quantity is then heated in a tall narrow glass upon the water-bath with a little water, adding gradually hydrochloric acid and potassium chlorate until the whole, after the larger particles have been crushed with a glass rod, becomes clear and thin, and any fat present collects on the surface. If too little fat is present a little pure butter fat is added. The mixture is diluted with hot water, well stirred up, and let stand until completely cold. Most of the hairs and other characteristic tissues will be found entangled in the fat, which is lifted off and examined with the microscope.

CORRESPONDENCE.

LARD.

To the Editor of the Chemical News.

SIR,—I should not have troubled you with a further letter upon this subject were it not for the following facts:—I was turning over the pages of vol. lli., 1885, of the CHEMICAL NEWS when I came across "Notes and Queries," under which head (dated April 2, 1885), was "Watered Lard;" this is signed "W. Brown," and, without wishing to create further correspondence on the matter, I should like those few remarks in "Notes and Queries" to be compared with what I have already written. What I have previously said is light itself on this matter of "lard." I reiterate that the whole of the fat of the hog melted down is nothing more or less than pork dripping, and to bring it up to anything like proper lard it is mixed with other substances and sold as "Refined Leaf Lard." The above reference proves that it is done. It is but five years ago that it troubled someone to ask those who had to deal with such adulterations to endeavour to put a stop to such matters; yet we find, when I interest myself in the question, that it brings forth a reply which, I contend, is simply saying lard (?) and all things are pure.

I commenced this correspondence with no other object whatever than of pointing out what my experience of lard had been during the last thirty years. We have, "like the poor," sophisticators always with us, but should we allow them to follow their ways without taking some action to counteract their *modus operandi*. My remarks hitherto have not, I see, been without effect; for it seems that some of my statements have been transferred to the *Grocer*, and, of course, all against my ideas.

I am obliged to you, Mr. Editor, for the insertion of my former letters, and, in conclusion, trust that Mr. Allen, of Sheffield, and others would thoroughly corroborate all I have written respecting "lard."—I am, &c.,

JOHN H. SWINDELLS, Ph.D., D.Sc.

13, Keogh Road,
Maryland Point, Essex.

LARD.

To the Editor of the Chemical News.

SIR,—I have read the letters which have appeared in recent numbers of the CHEMICAL NEWS on the subject of lard. Permit me to state, for the benefit of your readers who may be interested in this subject, that the United States Department of Agriculture, Division of Chemistry, has recently made a series of studies on lard and lard adulterants. The result of these studies is presented in a Bulletin, in which, to quote the words of the Chemist of the Department, "It is believed that the present state of our knowledge of lard and its compounds is fully set forth." This Bulletin is known as "No. 13, Lard and Lard Adulterations." It may be obtained, gratis, I believe, on application to the Department of Agriculture, Washington, D.C., United States of America.—I am, &c.,

J. T. DONALD, M.A.

124, St. James Street, Montreal,
March 11, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 9, March 3, 1890.

Absorption of Atmospheric Ammonia by Vegetable Soils.—Th. Schloesing.—The author, as far back as

1876, concluded that in the exchanges of ammonia between the atmosphere and the soil the latter is the gainer, and acquires, in this manner, quantities of ammonia which are not unimportant. Lately, this conclusion has been contested. Not only doubts have been raised on the origin of the ammonia acquired by soils exposed to the air, but it has been urged that the property of absorbing the ammonia of the air, though admissible in acid soils, cannot exist in calcareous soils. In a series of experiments with different soils there has been found in every case a gain of total nitrogen. A series of further experiments, announced as to appear in the author's next communication, will show that the presence of limestone does not interfere with the fixation of atmospheric nitrogen.

A Contribution to the Chemical Study of the Truffle.—Ad. Chatin.—The riches of the truffle in phosphoric acid, lime, and magnesia is remarkable in comparison with the poverty of the soils. Six elements, nitrogen, phosphorus, potassa, lime, iron, and sulphur, appear characteristic of the truffle. The author considers that the nitrogen is derived in great part from the air confined in the soil. Phosphoric acid forms a mean of more than 50 per cent of the ash of the truffle, and it is closely followed by potassa. Lime forms 7—8 per cent of the ash, whether the earth contains 50 per cent of calcareous matter or scarcely 1 per cent. The proportion of iron oxide is about 5 per cent. Soda is present to about 1 per cent, but rises in some cases to 6 per cent. Magnesia rises and falls along with soda. Manganese is present in all truffles, as are chlorine and iodine.

Historical Note on Batteries with Melted Electrolytes.—Henri Becquerel.—The author shows that the system of batteries proposed by M. Lucien Poincaré is not novel. Electric currents have been obtained by using a salt in fusion as one of the electrolytes by A. C. Becquerel thirty-five years. They have been also proposed by M. Jablockhoff, in 1877, by M. Brand in 1882, and by MM. Fabringi and Farkas in 1888.

The Vapour-Density of the Selenium Chlorides.—C. Chabré.—The vapour-density of the chloride SeCl_4 at 360° is 3.86; calculation gives 3.84. In opposition to Messrs. Evans and Ramsay he concludes that 2SeCl_4 is resolved into $\text{Se}_2\text{Cl}_2 + 3\text{Cl}_2$.

Certain Derivatives of Erythrite.—E. Grimaux and Ch. Cloez.—The derivatives studied are hydrofurfuran and the erythrite bromhydrines.

Derivatives of Heptamethylene.—M. Markownikoff.—Not adapted for useful abstraction.

The Preparation and Properties of Aricine.—H. Moissan and E. Landrin.—The arica bark operated upon contained neither quinine nor cinchonine. The base obtained is insoluble in water, soluble in alcohol at 90° and in ether. It melts at 188° — 189° . Its melting-point and rotatory power ($-58^\circ 18'$ in an alcoholic solution) distinguish it clearly from its isomer, cusconine.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 1.

On the Constitution of Manganese Peroxide.—W. Spring and M. Lucion.—Manganese peroxide should not be represented by the formula MnO_2 , but by Mn_2O_4 , and it is very probably a manganous manganate MnO, MnO_3 , or a manganese permanganate $\text{Mn}_2\text{O}_3 \cdot \text{MnO} = 5(\text{MnO}_2)$.

Memoir on an Application of Thermochemistry.—Albert Colson.—The author determines the solution- and neutralisation-heats of the bases piperidin, pyridin, and nicotin, and draws conclusions as to the properties and the constitution of nicotin. He finds that nicotin possesses a powerful basicity of the order of ammonia and another very faint basicity which scarcely acts upon dimethyl orange when the liquids are diluted.

MISCELLANEOUS.

Analogies between Music and Chemistry.—In the *Chemiker Zeitung* there has appeared a paper on this subject, which can be reproduced only by special permission, and which is intelligible only to persons who are at once chemists and musicians. We, therefore, merely call attention to its occurrence.

Chemical Manufacturers and their Workmen.—At the annual meeting of the Oldbury Alkali Works Provident Society (Messrs. Chance Bros.), held at the works, on Saturday, Mr. A. M. Chance, one of the partners, and manager of the firms' extensive works, laid before the operatives an interesting scheme. He explained that the firm had purchased four acres of land at a place named Tal Bank, for workpeople to build houses on. He (the speaker) and another member of the firm had been appointed trustees, and the disposal of the land was left in their hands. They invited those workpeople who chose to build their own houses to consider the matter, so that some feasible plan of dividing the land might be devised. The workmen could either purchase the freehold of the land or take it on a long or short lease. A committee, consisting of Messrs. A. M. Chance, G. F. Chance, and five workmen, was appointed to consider the building scheme. Mr. Chance intimated that if the proposal was appreciated the firm would assist their workpeople in another direction.

ERRATUM.—P. 136, in table, for "Br 26" read "Br 29."

MEETINGS FOR THE WEEK.

MONDAY, 31st.—Medical, 8.30.

Society of Chemical Industry, 8. "A Separation for Solids and Liquids," by Dr. W. S. Squire. Wool-washing and Wool Fat and Products," by H. Langbeck.

TUESDAY, April 1st.—Institute of Civil Engineers, 8.

Pathological, 8.30.

THURSDAY, 3rd.—Chemical, 8.

Mathematical, 8.

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W. FRESENIUS, Ph.D.
E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
Experimental Physics W. FRESENIUS, Ph.D.
Stoichiometry E. HINTZ, Ph.D.
Organic Chemistry
Chemical Technology E. BORGMANN, Ph.D.
Microscopy, with exercises in Microscopic work

Chemistry and Analysis of Foods Prof. H. FRESENIUS, Ph.D.
E. BORGMANN, Ph.D.
W. FRESENIUS, Ph.D., and
E. HINTZ, Ph.D.

Hygiene Dr. med. G. FRANK.
Practical exercises in Bacteriology
Technical Drawing, with exercises J. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL's Verlag, at Wiesbaden, or to the undersigned.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1584.

PROFESSOR GRÜNWALD'S MATHEMATICAL SPECTRAL ANALYSIS.

[Most of our readers will be aware that Prof. Grünwald has been led, by a mathematical examination of the spectra of hydrogen, oxygen, and some other elements, to the conclusion that these bodies are compounds. This view has been subjected to a very hostile criticism by Dr. H. Kayser in the *Chemiker Zeitung* (1889, No. 13, pp. 1655 and 1687), mainly on the ground that the coincidences of the spectral lines are merely what the doctrine of probabilities would lead us to expect. To this criticism Prof. Grünwald has replied in the *Chemiker Zeitung* (1890, vol. xiv., No. 20). The substance of his reply we lay before our readers.]

On May 9, 1887, the author foretold to Prof. Liveing, of Cambridge, a long list of lines which, according to his theory, should be found in the spectrum of water, requesting Prof. Liveing to examine this spectrum very closely, to measure even the faintest lines, and to test the accuracy of his predictions. The coincidence was most surprising.

Dr. Kayser, setting out with the assumption that the theory was merely a structure of artificial hypotheses, resting merely on the above-named result, fell to work to submit the author's publications to a—as he thought—destructive criticism, and in particular to show that the above coincidences were merely accidental. To this end he adduced a calculation showing that the number of coincidences was up to about 0.5 Angstrom unit, the same as might have been expected from a purely arbitrary assumption of the wave-lengths predicted.

This calculation, however, proves nothing, because Dr. Kayser takes into account merely the number, and not the kind and the degree of accuracy of the coincidences. He ignores how many complete coincidences occur between 0 and 0.1, 0.1 and 0.2 Angstrom unit, &c. But, even assuming the calculation as correct, it would be a logical error to argue from the mere probability of a certain number of coincidences up to 0.5 Angstrom units to the necessity of this number, still more, as Dr. Kayser curiously does, to the necessity of the existing very close coincidences. How much the probability of mere accidental coincidences depends, not merely on their number, but on their kind, will be very plainly seen on supposing that the numbers of the one series were (with the same number and distribution of coincidences) all smaller or greater, say by 0.5 Angstrom unit, than the corresponding numbers of the other series. Dr. Kayser's calculation would then still remain the same, though the probability that the coincidences were accidental would be very trifling.

Further, a physical cause tends to decrease the number of the experimentally demonstrable coincidences. The rays of the spectrum of water-vapour corresponding to the fainter, and especially to the more refrangible rays of the second hydrogen spectrum, are exceedingly feeble, so that no calculation of probabilities can determine and take into account how many coincidences may in this manner escape observation.

Love's graphic method of distinguishing the accidental from the necessary coincidences of two spectra is not false, as Dr. Kayser alleges, but it is, on the contrary, correct under suppositions which in many cases are admissible, and it is the only method at present known which considers not merely the number but the degree of accuracy of the coincidences. The conditions of its ap-

plicability will appear from the following demonstration:—

Let $\lambda = \lambda_1, \lambda_2, \lambda_3 \dots$ and $\lambda' = \lambda'_1, \lambda'_2, \lambda'_3 \dots$ be two corresponding or approximately identical series of wave-lengths, which are supposed to belong to one and the same substance, so that two corresponding numbers, $\lambda = \lambda_1$ and $\lambda'_1 = \lambda'_1$, are slightly different only from errors of observation, whilst their true values are identical.

Let all numbers of the same series be of equal value (in point of observation), and let the value of the numbers λ of the first series be to the value of the numbers of the second series as $m : m'$.

Then—

$$\frac{m\lambda + m'\lambda'}{m + m'}$$

is the probable value of the corresponding inaccurate numbers λ and λ' , and—

$$\frac{m\lambda + m'\lambda'}{m + m'} - \lambda = \frac{m'(\lambda' - \lambda)}{m + m'} = \gamma(\lambda' - \lambda);$$

$$\gamma = \frac{m'}{m + m'}$$

is the probable value of the error in λ . We find thus—

$$\gamma(\lambda'_1 - \lambda_1), \gamma(\lambda'_2 - \lambda_2), \gamma(\lambda'_3 - \lambda_3) \dots$$

as the probable errors of the figures $\lambda_1, \lambda_2, \lambda_3$, of the first series in case both these and the second series belong to the same substance, as it is suspected.

We further suppose that the probability of any given possible error in the numbers of either series is independent of the magnitude of the single wave-lengths, so that it might have occurred with equal probability in the determination of one wave-length as of all the others of the same series.

The errors $\gamma(\lambda' - \lambda) = \gamma(\lambda'_1 - \lambda_1), \gamma(\lambda'_2 - \lambda_2) \dots$ could as easily occur in successive determinations of one and the same wave-length, and the probability that an error $s = \gamma(\lambda' - \lambda)$ lies between s and—

$$s + ds = \gamma(\lambda' - \lambda) + \gamma.d(\lambda' - \lambda)$$

would be equal to—

$$\frac{h - h e^{-h s^2}}{\sqrt{\pi}} e^{-h s^2} ds$$

where $ds = -\gamma d(\lambda' - \lambda)$ is a constant minimal difference in error, independent of s . The number, γ , of the cases proportional to this probability in which such an error occurs must consequently be represented by an equation of the form—

$$y = b e^{-h s^2} = b e^{-h \gamma^2 (\lambda' - \lambda)^2} = b e^{-\beta s^2}$$

if $\lambda' - \lambda$ is put $= x$, and $\beta = h\gamma^2$ and b denote constants.

The number of cases in which an error $s = \gamma x$ occurs between γx and $\gamma x + \gamma dx$ is equal to the number of cases in which the deviation x lies between x and $x + dx$. If, therefore, the near coincidences between the two series are not accidental but real, it must then be expected, according to the principles of the calculus of probabilities, and under the above suppositions, and between the number γ of the cases in which the deviations x of the corresponding numbers of the first and second series lie between x and $x + dx$, there must exist approximately a relation of the form $y = b e^{-\beta x^2}$, where dx represents the smallest possible constant alteration of the variable deviation x .

Love's graphic method, depending on the last equation, is consequently, under the suppositions above mentioned, accurate and applicable.

(To be continued).

A New Bismuth and Potassium Iodide.—L. Astre. —This salt, when isolated by means of acetic ether, answers to the formula $(\text{BiI}_3)_2\text{KI}$, and not to that given by Nickles.—*Comptes Rendus*, Vol. cx., No. 9.

THE ACTION OF CHLORINE ON HÆMATOXYLIN AND THE EXTRACTIVE MATTER OF LOGWOOD.*

By WM. W. MACFARLANE and PHILIP S. CLARKSON.

It is well known among dyers, who have had any experience in extracting the colouring-matter from logwood by boiling the wood under pressure in closed vessels, that a larger quantity of wood, when so treated, is required for dyeing a given quantity of material, than when the colouring matter is extracted by boiling the wood in an open vessel, such as a dye-tub. It was the desire to discover the cause of this difference, and to avoid the loss of colouring matter, that led to a long series of experiments, and the discovery that chlorine can be used to increase the dyeing power of the extractive matter of logwood; and also that hæmatoxylin and hæmatein have entirely different values for the dyer, depending upon the manner in which they are used; that is, whether used for colouring wool or cotton, and whether the dyeing is done in an acid, alkaline, or neutral bath.

Logwood, before it is used by the dyer, is treated by a process called "curing," which consists in saturating the chipped or ground wood with water, then allowing it to lie in heaps or beds until a kind of fermentation or heating takes place. It is then necessary to move it frequently to avoid any considerable increase in temperature, and to expose all portions of it to the oxidising influence of the air. Exactly what takes place in this curing process is not known, as the composition of the extractive matter of logwood has not been determined. It is known that the wood contains hæmatoxylin, and it is supposed that certain glucosides are present, which, during the process of curing are broken up, yielding hæmatoxylin or hæmatein. Hæmatein is produced during this process, as will be shown later. Wood which has been subjected to this treatment, although it contains from 10 to 25 per cent more water, gives the dyer much better results, particularly on wool, than an equal weight of the wood in the condition it comes from the chipping or grinding machines.

For a long time attempts have been made to develop, or increase, the dyeing power of the extractive matter of logwood, either during the extraction process, or after the extractive matter had been obtained in an aqueous solution. Most of the substances used for this purpose are oxidising agents, and are used probably with the idea of converting hæmatoxylin into hæmatein. In 1885, C. E. Avery obtained a United States patent for the oxidising of logwood liquors or extracts by the action of "oxidants such as a solution of bleaching-powder, hypochlorous acid, chloric acid, chlorates, or nitrates of the alkalies and alkaline earths." He further claims the use, for this purpose, of "oxidising substances, such as solutions of chlorates of potash, or lime, or nitrates of potash, soda, or lime, which, whilst mixing with the logwood liquor at moderate temperatures, oxidise slowly or not at all, but on raising the temperature, particularly under pressure, or by the addition of acid or acid salts, become oxidisers of hæmatoxylin to hæmatein." In the specification of this patent, the quantity of a chlorate or nitrate necessary to convert a given quantity of hæmatoxylin is stated, but no directions are given as to the quantity of bleaching-powder or hypochlorous acid to be used to effect the desired result. The authors made many experiments, both following closely the specification of this patent, and with variation of the quantity of oxidants, and of the method of using them, but were not able to obtain any results which would pay for the labour and material used. In using a solution of bleaching-powder for this purpose, it was assumed that the combined or available chlorine was the oxidising agent intended to convert the

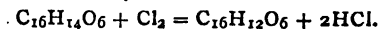
hæmatoxylin to hæmatein, and although many experiments were tried, the result was invariably a dull grey shade of black.

In Wurtz's "Dictionnaire de Chemie" (vol. i., Pt. 1, p. 645) it is stated that chlorine converts hæmatoxylin into a brown amorphous mass. Erdmann (*Jour. für Prakt. Chemie*, xxvi., 202), Reim (*Berichte der Deut. Chem. Gesell.*, 1871, p. 329), and Dralle (*Ber. der D. Chem. Gesell.*, 1884, p. 372), found that no definite and separate compounds were formed by the action of chlorine on hæmatoxylin. After many fruitless experiments, and when all probable means of producing the desired result had been tried, it was determined to make some experiments, using free chlorine added in the form of an aqueous solution, to the solution of the colouring matter. For this purpose a dilute aqueous solution of the extractive matter of cured wood was used. The results were determined by making dyeing tests in the mixed solutions with skeins of woollen yarn mordanted with potassium dichromate and potassium bitartrate. The results were surprising, and showed that the depth of colour increased with the amount of chlorine used, until a maximum quantity was reached, when any further increase in the quantity of chlorine produced a dull and grey shade. After further experiments, it was found that by using a 42° extract of logwood, which had undoubtedly been made from dry cut wood, that is, wood not subjected to the curing process, and chlorine equivalent to about 9 per cent of the weight of the extract, the dyeing power of the colouring matter was increased 150 per cent.

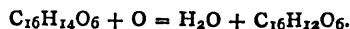
Owing to the difficulties experienced in making and handling large quantities of chlorine-water, it was found necessary to devise some other means of treating the extractive matter with the chlorine. Very good results were obtained by circulating the solution of the extractive matter through any suitable vessel, so arranged as to expose as large a surface of the solution as possible, and into this vessel the chlorine gas was delivered from the generator. The quantity of chlorine used was regulated by the quantity of materials placed in the generator. Later, it was found that if, during the absorption of the chlorine, the temperature of the solution was maintained at about 80° C., less chlorine was required to produce the desired result than when the action took place at the ordinary temperature.

It has been stated that by increasing the colouring power of the logwood by the use of oxidising substances, the colours obtained are not fast on exposure to light and air. In practice, however, it was found that a sample of worsted cloth dyed black on chromin mordant with logwood extract developed with chlorine, after an exposure of six weeks, had not undergone any more change in shade than a sample dyed with ordinary cured wood.

In order to ascertain the exact chemical change which takes place in the hæmatoxylin in this process, a sample was obtained, manufactured by E. Moerk, and treated in the same manner as the extract. First, to determine the amount of chlorine necessary to yield the greatest dyeing power, samples were treated with varying amounts of chlorine and dye tests made. It was found that the greatest development was obtained when the proportion of chlorine was four atoms to each molecule of hæmatoxylin, which is equal to forty-seven per cent of the hæmatoxylin. This would indicate a more complex reaction than the conversion of hæmatoxylin to hæmatein, as that would require but two atoms of chlorine for each molecule of hæmatoxylin.



Avery, in his patent, calculates the amount of oxidising agents necessary, on the basis of the simple reaction—



This constitutes a marked difference in the two processes. A larger quantity of chlorine renders the shade dull and grey.

* Read at the Chemical Section of the Franklin Institute, January 21, 1890.

It is stated by various authorities, especially by Dralle (*Berichte*, 1884, Feb., p. 372), that no separable compounds are obtainable by the action of chlorine on hæmatoxylin and that hæmatoxylin is not formed in the reaction. An attempt was made to determine the products of this action, and a larger quantity of hæmatoxylin was treated with the proportional amount of chlorine, viz., four atoms of chlorine to each molecule of hæmatoxylin. The method used was to dissolve the hæmatoxylin in hot water, allow it to cool and then treat with chlorine-water containing the calculated amount of chlorine gas. By repeated washing with ether, containing a small portion of alcohol, and distilling off the ether and drying, there was left a brownish resinous mass, completely soluble in alcohol. By treatment of this residue with chloroform, a white crystalline substance was separated. This was soluble in ether, water, chloroform, and acetic acid. However, this was not obtained in sufficient quantity to determine the composition or characteristics. By further treatment of this residue with ether, two bodies were separated; one with a brownish resinous appearance, the other with a bright greenish metallic lustre. By saturation of the original solution with common salt, and again treating with ether, more matter was extracted, but was found to consist mainly of brown resinous matter. Since the method of saturating the solution with salt to separate the products of this reaction appears to have been used in former investigations, it is probably the cause of the statement that only resinous bodies, not admitting of purification, are the result of the action of chlorine on hæmatoxylin.

By carefully distilling the ether from the washing of the solution it is possible to separate most of the bronze substance before the solution is completely evaporated. It then separates in shining scales, which are apparently not crystalline. These contain small amounts of the resinous matter. By washing with ether several times, it is possible to obtain a bright greenish bronze body, with a strong metallic lustre. This gives a red, almost approaching violet, powder. Although seemingly pure, it contains a trace of chlorine, and has not been obtained sufficiently pure to warrant a determination of the composition by combustion. It is insoluble in cold water, somewhat more soluble in hot water, freely soluble in alcohol, almost insoluble in ether and chloroform. It has powerful dyeing properties, 5 per cent on wool giving a blue black. Therefore, in its physical characteristics and chemical properties, it is identical with hæmatein, and justifies the supposition that it is hæmatein. It is hoped to obtain this in a state sufficiently pure to make a determination of the composition.

The resinous substance is easily soluble in ether, alcohol, and water. It appears to be a chlorine substitution product of either hæmatein or hæmatoxylin, as the amount of chlorine contained in mixtures of this and hæmatein is in proportion to the amount of this substance. It remains in the dye-bath, after the hæmatein has been absorbed by the wool, and probably has no effect on the colour produced. The difficulty in completely separating these bodies lies in the fact that hæmatein is soluble in solutions containing the resinous matter; therefore, it is very difficult to obtain one entirely free from the other.

In order to have some standard of comparison with the colouring-matter of logwood after curing, a well-bronzed sample of wood was treated with alcohol. To this solution, which was brownish yellow, hydrochloric acid was added, and the whole distilled to a small volume. On cooling, there was an abundant separation of colouring-matter, which, after treatment with ether and alcohol, remained as a bronze powder. A combustion of this was made, which gave—

C		62.94	62.66
H		4.31	4.16
O		32.75	33.18

Erdmann found—

From this it is evident that this is the same as the hæmatein obtained by Erdmann by the oxidation of hæmatoxylin in the presence of ammonia.

On making comparative dye tests of the colouring-matter obtained by the action of chlorine on hæmatoxylin and this extracted from cured wood, the colours obtained were very similar in depth and shade; that of the hæmatein from wood being slightly duller. Both were about double the colour obtained with hæmatoxylin. With the latter it is very doubtful if any deeper shade than a very light blue would be obtained if the air were entirely excluded from the bath; the shade constantly growing deeper in proportion to the time the dyeing is continued, while with hæmatein the bath is exhausted in a comparatively short time, and no further increase of colour occurs.

In practical dyeing there are several methods in use which are practically different; wool dyeing being carried out in a neutral or slightly acid bath at 100° C.; cotton dyeing, commonly in a slightly alkaline solution, and what is known as speck-dyeing, in a strongly alkaline solution containing caustic alkali at a temperature below 15° C. Speck-dye is used to colour the cotton in mixed goods after the wool has been dyed, or to colour the burrs and other vegetable substances which may have become mixed with the wool. The low temperature is employed to prevent the wool absorbing any colour during the operation. From the differing conditions it was considered probable that varying results would be obtained from the use of the same colouring-matter in each of these methods. In the experiment with wool, equal weights of woollen yarn were taken and mordanted with three per cent potassium dichromate and two per cent of potassium bitartrate. These skeins were then dyed with five per cent each of hæmatoxylin, hæmatein from cured wood, and hæmatein obtained with chlorine. The operation was carried on at a boil for one hour. The shade given by the two hæmateins was at least twice as full as that obtained from hæmatoxylin. Next some speck-dye was made of the same substances in the following proportions:—5 per cent colouring-matter, 44 sodium carbonate, 5 sodium hydrate, 1 of sodium sulphite, and 16 of copper sulphate; each dissolved in water, the solutions mixed, made up to equal volumes, boiled, and allowed to cool. The skeins of unmordanted cotton yarn of equal weights were then dyed in these baths. In this case the shade obtained with hæmatoxylin was much darker than with the hæmateins; these being of little practical value. There was a marked difference in the appearance of the baths, that of the hæmatoxylin being of a deep purple colour, with little or no precipitate, the other two of a blue colour, with much precipitate.

Noticing a yellowish colour in this precipitate, which might have been due to the reduction of the copper, the action of each of these substances was tried on Fehling's solution. It was reduced by hæmatoxylin much more slowly than by hæmatein; but it was found that more copper was reduced by the hæmatoxylin than by the hæmatein. 50 m.grms. of hæmatoxylin gave 0.1675 grm. Cu₂O, and the same quantity of hæmatein, 0.1541 grm. Cu₂O. These may not be the constant reduction proportions, as this was not tried under varying conditions; but these figures were obtained by treating the bodies with an excess of Fehling's solution. A farther report will be made on this subject. From these experiments it would appear that when alkaline solutions are used in the application of logwood, the extract or decoction should be made of dry cut wood, while for wool much better results are obtained by the use of cured wood.

On finding that free chlorine in proper proportions would increase the dyeing powers of logwood extract, and that an excess produced dull and grey shades similar to those obtained by the use of bleaching-powder or calcium hypochlorite, the experiment was tried of reducing the amount of the calcium salt to about half the theoretical quantity. When this was done a marked increase of

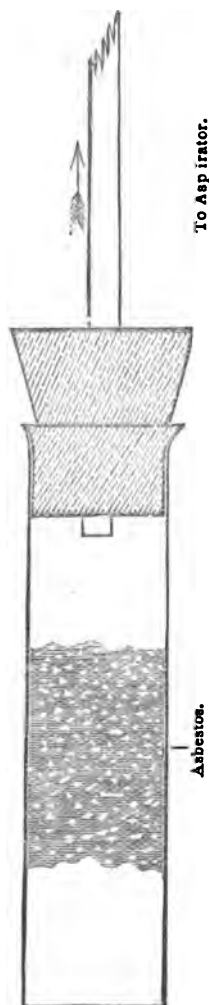
colour was obtained, with no deterioration in shade. It has been shown that the greatest development of the dyeing power of hæmatoxylin results when 47 per cent of free chlorine is used; but when a solution of bleaching-powder is employed, the same effect is produced when the proportion of available chlorine to hæmatoxylin is but 23½ per cent.

MILK ANALYSIS.

By FRANCIS WALLS, F.C.S., Government Analyst, Antigua.

THE following modification of the Adams process of milk analysis has been employed by the writer for some time with good results, and has worked satisfactorily in other hands.

In place of the blotting-paper coil, a tube containing asbestos is employed—a test-tube 18 to 20 m.m. wide with the bottom cut off, leaving a tube about 80 or 90



Drawing of Tube (real size).

m.m. long, is packed with long-fibre asbestos in its middle portion, the asbestos occupying rather more than one third of the tube; the asbestos being ignited before being used. The tube thus prepared is carefully weighed;

about 5 c.c. of milk are next run on to the asbestos, avoiding soiling the sides of the tube with the milk. The tube and milk are then weighed to ascertain the quantity taken. The tube with its contents are placed in a water-jacketed drying oven, heated to 100° C., into which passes a tube connected with an aspirator, and the milk tube is attached to the aspirator tube by means of a suitable cork. A steady current of air is drawn through the milk, which is thus speedily evaporated to dryness, and when thoroughly dry the tube is weighed to ascertain the total solid matter dried at 100° C.

The total solid matter being ascertained, the tube is transferred to a Soxhlet's extractor, the fat extracted by a suitable solvent and weighed in the usual manner. When the extraction is complete, the tube is again dried in the water-bath and again weighed, thus giving a direct estimation of the non-fatty solids, which can be checked by deducting the weight of the fat from the total solids; the weights thus ascertained will usually agree to about a m.grm. or 0.02 per cent.

This method possesses several advantages over the Adams method, though involving the same principle. The preparation of the tube occupies less time than that of an Adams coil, and requires no previous extraction with solvents to fit it for use. Being of less hygroscopic material, and not liable to loss of substance in handling, it admits of the total and non-fatty solids being determined on the coil itself, thus permitting the whole analysis to be performed on one portion of the milk, affording a direct, instead of differential, determination of the most important constituent—the non-fatty solids—and at the same time enabling the operator to check his results, which is impossible when determining total solids in one portion and fat by the Adams coil, and non-fatty solids by difference.

The following examples are taken as showing results obtained in ordinary practice:—

	I. Grms.	II. Grms.
Weight of tube and milk	12.549	10.7262
„ tube alone	6.293	5.7637
Weight of milk	6.256	4.9625
Weight of tube and dried milk..	7.127	6.2778
„ tube	6.293	5.7637
	0.834	0.5141
Weight of tube and non-fatty solids	6.839	6.0570
Weight of tube	6.293	5.7637
	0.546	0.2933
Weight of non-fatty solids	0.546	0.2933
Weight of flask and fat .. .	35.060	34.9920
„ flask	34.771	34.7727
	0.289	0.2193
Weight of non-fatty solids..	0.546	0.2933
„ fat	0.289	0.2193
Sum of non-fatty solids and fat	0.835	0.5126
Weight of non-fatty solids and fat determined di- rectly	0.834	0.5141
Difference	0.001	0.0015

Decomposition of Lead Hyposulphite by Heat.
Lead Triithionate.—J. Fogh.—The decomposition of lead hyposulphite by heat gives rise to a thermic phenomenon which is almost null, whilst the ulterior redissolution of the lead salt would absorb — 3 cal.—*Comptes Rendus*, Vol. cx., No. 9.

NEW GENERAL REACTION FOR NITROGEN IN ORGANIC SUBSTANCES.

By Prof. E. DONATH.

KJELDAHL's method for determining the nitrogen in organic bodies has now established itself in nearly all laboratories, since some modifications have rendered it applicable to almost all groups of bodies. The explanations hitherto proposed for the transformation upon which this method is founded are not very satisfactory. The author believes that this transformation may be more easily explained if we regard it with reference to the third thermo-chemical theorem, according to which every chemical change which ensues without the intervention of any foreign power (heat, electricity, light, &c.) always tends to form those bodies which, under the existing circumstances, evolve the greatest quantity of heat.

Every nitrogenous organic substance, on heating with concentrated sulphuric acid, undergoes a more or less thorough decomposition. In consequence, the positions of equilibrium of all the atoms are disturbed, and they are rendered more susceptible of entering into new combinations. If, at the same time, an energetic oxidising agent is present (permanganate, mercuric oxide, &c.), as in Kjeldahl's process, carbon and a part of the hydrogen are burnt, whilst the atoms of nitrogen which may be regarded as in the nascent state combine with a corresponding number of atoms of hydrogen to that system on whose union with the decomposing body (*i.e.*, sulphuric acid) the greatest liberation of heat will ensue. This is ammonia, the simplest compound base. If this inference is correct, then inversely, if the decomposition of a nitrogenous organic body is effected by a powerful base in presence of an oxidising agent, the nitrogen should not pass into combination with hydrogen, but with oxygen, forming an acid, and indeed that acid on whose neutralisation by the decomposing base the maximum of heat is liberated. This must therefore be either nitrous or nitric acid, in which form the nitrogen must appear on the above described decomposition of nitrogenous organic matter.

The neutralisation-heat of nitrous acid with potassa-lye is not to be found in the most competent manual of the subject, Julius Thomsen's "Thermo-chemical Researches." But if we may conclude from an analogy (not in chemical constitution, but in the stage of oxidation) between phosphorous and nitrous acids, the neutralisation-heat of nitrous acid would be rather greater than that of nitric acid. Direct experiments have shown that nitrous acid, although a powerful reducer, does not destroy the colour of permanganate when boiled in an alkaline solution. This corresponds to the behaviour of oxalic acid, which reduces permanganate in an acid but not in an alkaline solution, because the neutralisation-heat of oxalic acid is greater than that of any organic acid which can possibly be formed. In the reduction of organic substances by energetic oxidation in an alkaline solution the nitrogen should appear as nitrous acid.

The experiments which the author has performed with a number of substances belonging to the most different groups have almost completely confirmed this supposition. The substances named below were introduced into small flasks in quantities of from 0.03 to 0.05 gm. (according to the proportion of nitrogen) with 0.5 to 1 gm. powdered permanganate, and from 15 to 20 c.c. of potassa-lye perfectly saturated at the ordinary temperature were added and heated to a boil, adding, if needful, as much more permanganate, until, on further boiling, the liquid remained violet or greenish blue. The flask was then let cool, the liquid moderately diluted with water, which occasions heating; the excess of permanganate is reduced by the addition of a few drops of pure alcohol, and the manganese hydroxide is filtered off. The filtrate is then tested by the admixture of freshly prepared solution of

potassium iodide and acidulation with hydrochloric acid, by means of carbon disulphide or zinc iodide and starch.

In addition, the filtrates were tested for oxy-acids in general by means of diphenylamine in a sulphuric solution, and for nitric acid in particular with brucine and concentrated sulphuric acid.

These experiments showed that in all the substances examined the reactions for nitric acid were produced with the greatest distinctness, but that the brucine and sulphuric reaction for nitric acid did not succeed in all cases. In the case of coal, potassium ferrocyanide, and all bodies of the aromatic group the reaction was more difficult and tedious.

The bodies examined were:—Urea, albumen, potassium ferrocyanide, amygdaline, indigotine, coal, pepsine, quinine sulphate, magenta, binitrobenzol, tropeoline, betaine hydrochlorate, asparagine, ammonium sulphate, casein, Biebrich scarlet, binitronaphthalene, naphthylamine, nitrosonaphthol, and nitrosotoluol.

As these bodies belong to nearly all the most important groups of organic bodies, the conclusion is justified that the above-described oxidation with permanganate and strong potassa-lye, and the consequent formation of nitrous acid, is a new universal reaction for nitrogen in organic compounds.—*Chemiker Zeitung*.

[The reader cannot fail to be struck with this paper. By heating nitrogenous matter with alkaline permanganate, Prof. Donath appears to convert more or less of the organic nitrogen present into nitrous acid. Now, Mr. Wanklyn and the numerous chemists who have used his method of water analysis by the very same treatment, obtain a large proportion of the organic nitrogen in the same substances in the form of ammonia. Prof. Donath does not appear to have made any quantitative determinations, and, on the other hand, we do not find that Mr. Wanklyn has put on record any observations affirming or denying the production of nitrous acid by the action of alkaline permanganate upon nitrogenous bodies. Both Prof. Donath and Mr. Wanklyn find potassium ferrocyanide the most refractory body.—*Ed. C.N.*]

THE VOLUMETRIC DETERMINATION OF FREE HALOGENS AND THE DETERMINATION OF IODIDES IN PRESENCE OF CHLORINE AND BROMINE.

By P. LEBEAU.

FOR the volumetric determination of iodine in a liquid containing bromine and chlorine the iodine is displaced by dilute nitrous acid in excess and the solution is then poured into carbon disulphide. The violet solution is then decolourised by standard stannous chloride. This method, indicated by Fresenius, is useful, but very tedious, since the iodine must be completely dissolved out by the carbon disulphide, the coloured solution must be transferred to another flask to avoid the action of the nitrous vapours upon the standard solution, and the liquid must finally be washed to remove any traces of nitrous acid.

The author, having to make a great number of exact determinations of the halogens, has sought for a method more precise and more expeditious. To this end he has sought to render visible the limit of the displacement of iodine by bromine, this reaction being the simplest and most certain, and he has finally adopted a procedure based at once upon the colouration of carbon disulphide by iodine and the decolouration of extract of indigo by bromine. There are thus two colour-indications in juxtaposition, easy of comparison, and one of which is annulled at the end of the titration.

Into a flask holding about 200 c.c. there are put 30 to

40 c.c. of carbon disulphide and as much distilled water, and then a known volume of the iodised solution to be examined. A few drops of indigo extract are then added. Standard bromine-water is then dropped in from a burette with a glass tap, stirring briskly. The iodine set free dissolves in the carbon disulphide, which turns violet, and the supernatant liquid remains blue until a drop of bromine-water in excess decolourises the extract of indigo. The end of the reaction is very distinct.

The bromine liquor used is very convenient, but some precautions are necessary to keep its value from varying. Stoppers and joints of caoutchouc must not be used, and the reagent must be transferred directly from the stoppered bottle to a burette with a glass cock. Bromine being very volatile, the strength of bromine-water, when once known, cannot be assumed as permanent. Before each series of assays the relative value of the bromine-water must be established by means of a solution of pure potassium iodide of known strength.

In these determinations the value of the bromine-water was fixed in an independent manner without making use of iodides. The author found it convenient for determining chlorine, bromine, and iodine in solution to convert them into the corresponding zinc salts, and thus to bring their determination to a titration by means of a solution of silver. To this end the liquid containing the free halogen is introduced into a stoppered flask with the addition of a few grms. of pure zinc powder. Almost immediately the halogen disappears, forming neutral zinc bromide, and may be titrated with a silver solution, using neutral potassium chromate as an indicator.—*Comptes Rendus*, cx., p. 520.

REVISION OF THE ATOMIC WEIGHT OF GOLD.*

By J. W. MALLETT, F.R.S.,
Professor of Chemistry in the University of Virginia.
(Concluded from p. 153).

Calculation of Results.

In calculating the atomic weight of gold from the data furnished by the experiments which have been described, I have thought it best to conform to the most general usage of those who have been working on questions of this sort of late years, so as to facilitate comparisons with the results of others. Hence, although the atomic weight has been calculated separately from the figures of each experiment reported, the value deduced from each series has not been taken as the arithmetical mean of the separate results, nor has the probable error of these or of the mean been calculated by the method of least squares, as was done in my paper on the atomic weight of aluminium, but instead, the general result for each series has been obtained, as in the calculations of Meyer and Seubert, from the aggregate quantities of the materials employed, though I am by no means convinced that this mode of reckoning is in all cases sound in principle, giving, as it does, weight to each experiment in proportion to the quantity of material employed.

The atomic weights assumed for the other elements involved are those which have been most generally accepted in calculations of this kind, based for the most part on the experiments of Stas, and representing, with greatest probability, the values as at present known to us. They are as follows:—

H = 1.
Ag = 107.66.
Cl = 35.37.
N = 14.01.
C = 11.97.

Calculated Results.

The following are the values obtained for the atomic weight of gold from the different series of experiments:—

First Series.

(Ag₃: Au :: 322.98 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	12.4875	7.6075	196.762
II.	13.8280	8.4212	196.694
III.	11.3973	6.9407	196.688 Lowest value.
IV.	5.5286	3.3682	196.770 Highest "
V.	4.6371	2.8244	196.723
	47.8785	29.1620	196.722

Second Series.

(Ag₃: Au :: 322.98 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	13.5149	8.2345	196.789
II.	12.6251	7.6901	196.731 Lowest value.
III.	17.2666	10.5233	196.843 Highest "
IV.	4.5141	2.7498	196.746
V.	5.8471	3.5620	196.756
VI.	6.4129	3.9081	196.828
	60.1807	36.6678	196.790

Third Series.

(Ag₄: Au :: 430.64 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	12.4851	5.7048	196.772
II.	17.4193	7.9612	196.817 Highest value.
III.	5.3513	2.4455	196.799
IV.	9.1153	4.1632	196.685 Lowest "
	44.3710	20.2747	196.775

Fourth Series.

(N(CH₃)₃HCl₄: Au :: 201.40 : x).

Exper.	Loss by ignition of trimethyl ammonium auri-chloride. Grm.	Gold. Grm.	Atomic weight of gold.
I.	7.5318	7.3754	197.218
II.	7.8432	7.6831	197.289 Highest value.
III.	5.2811	5.1712	197.209
IV.	3.3309	3.2603	197.131 Lowest "
V.	2.8165	2.7579	197.210
	26.8035	26.2479	197.225

Fifth Series.

(Au: Au :: 107.66 : x).

Exper.	Silver. Grm.	Gold. Grm.	Atomic weight of gold.
I.	2.8849	5.2721	196.747
II.	3.4487	6.3088	196.945 Highest value.
III.	2.3393	4.2770	196.837
IV.	1.9223	3.5123	196.709 Lowest "
V.	2.0132	3.6804	196.817
	12.6084	23.0506	196.823

Sixth Series.

(H: Au :: 1 : x).

Exper.	Hydrogen. Grm.	Gold. Grm.	Atomic weight of gold.
I.	0.02053	4.0472	197.136
II.	0.02039	4.0226	197.283 Highest value.
III.	0.02079	4.0955	196.994 Lowest "
	0.06171	12.1653	197.137

Seventh Series.
(H₃: Au :: 3: x).

Exper.	Hydrogen. Grm.	Gold. Grm.	Atomic weight of gold.
I.	0.15768	10.3512	196.941
II.	0.12574	8.4525	196.894
III.	0.12345	8.1004	196.851
IV.	0.05016	3.2913	196.848 Lowest value.
V.	0.05306	3.4835	196.956 Highest "
VI.	0.05550	3.6421	196.865
	0.56559	37.1210	196.897

General Mean of Results.

If each of the foregoing series of experiments be represented by the result calculated from the aggregates of material used, and if equal weight be attached to the results of all the methods, the general mean derived from the whole of the 34 experiments will be as follows:—

First series	196.722	Lowest value.
Second „	196.790	
Third „	196.775	
Fourth „	197.225	Highest value.
Fifth „	196.823	
Sixth „	197.137	
Seventh „	196.897	
General mean	196.910	

The results of the fifth and sixth series, obtained by electrolysis are, I am convinced, much less entitled to confidence than any of the others. If these two be excluded, the general mean of the remaining series will be 196.882, a number differing but little from the mean of all.

The highest value is that derived from the fourth series—ignition of trimethyl ammonium auri-chloride. It has been seen that the individual results of this series agree fairly well with one another, and when examined in connection with the facts as to the different crops of crystals of the salt used, do not seem to present any evidence of want of uniformity in the material. But as it may still be suspected that traces of dimethyl or of monomethyl ammonium auri-chloride may have been present, and have caused the apparent value of the atomic weight of gold to come out higher than the truth, if we exclude also this series, the general mean of the remaining four will be 196.796.

Finally, if for the sake of comparison with the results of Krüss and of Thorpe and Laurie the general mean be taken for the first three series only, in which auric chloride and bromide were examined, the result is 196.762—intermediate between the general means of the two previous researches, but rather nearer to that derived from the work of Thorpe and Laurie than Krüss.

It will be observed that, although there is pretty close agreement among the means of results obtained by altogether different methods, this agreement is not so close as that presented by the results of the nearly similar methods pursued in the first three series. This cannot but suggest the probability of there being still sources of minute errors inherent in the methods themselves, and not dependent upon mere imperfections of manipulation in carrying these methods out. Although there is thus to be noticed a slight tendency on the part of each method to yield high or low figures severally with the exception of the results of the fourth series there does not appear to be any considerable reason to see in the values obtained confirmation of the special suspicions in connection with each method which have been stated. There is no clear evidence of any difference in the results which can be traced to the history of the particular samples of gold used; a larger number of somewhat low results seem to have been yielded by the metal designated as (C)—i.e., obtained from the United States Assay Office

at New York—than by the others, but the difference is not marked or constant enough to warrant any trustworthy conclusions as to the character of this material.

Concluding Remarks.

The atomic weight of gold, as deduced from the experiments reported in this paper, is entirely in accord with the place occupied by the metal in Mendeleeff's "periodic" classification of the elements, but this is equally true of the slightly different values obtained by Krüss, and by Thorpe and Laurie, and the only difficulty at one time apparent as to this point—namely, the relative positions of gold on the one hand and of platinum, iridium, and osmium on the other—has been removed, not by any change in the atomic weight of gold, but by changes affecting the values to be assigned the three other metals, as these values have been determined by Seubert.* It is very desirable that, in order to a fuller and more exact examination of the Mendeleeff table of the elements, there be accomplished as soon as possible a general revision of the atomic weights of all the elements of well determined individuality, so many of which are still very imperfectly known.

As to any bearing of the results of the present paper on the so-called hypothesis of Prout,† the general mean of all my results, or even the general mean with exclusion of the values obtained by electrolysis, approaches the integer number 197 rather more nearly than does the final number arrived at by Thorpe and Laurie, and still more nearly than does that considered by Krüss to express the final result of his experiments. If the results of the fourth series be also rejected, my general mean will be nearer the integer than is the Krüss number, but not quite so near as that of Thorpe and Laurie. I feel that somewhat greater confidence may be placed in my own work, simply on the ground of its involving the use of more completely different and independent methods—a principle which I believe to be of the first importance in any attempts at increased accuracy in the determination of atomic weights.

At the same time, as has already been pointed out, this work seems to me to furnish some probable evidence that not all inherent defects of method have been eliminated. Whether or not such defects may exist to an extent sufficient to account for the remaining difference between the value obtained and the integer multiple of the atomic weight of hydrogen there does not seem to be ground on which to express a positive opinion. But this research does not supply any clear evidence contradictory of such a possibility.

On this point, and generally on the attainment of what is sometimes rather too easily spoken of as the greatest possible accuracy in the determination of an atomic weight—particularly of an element for which the value is as high as that for gold—anyone who actually works in a conscientious way at such determinations will be pretty sure to feel more strongly the difficulty of the task, and to express himself with more caution, than do some compilers of results in assuming at any time that the last word has been spoken.

Decrease of the Fermentive Power of Ellipsoidal Yeast in Presence of Salts of Copper.—A. Rommier. —In case of vineyards yielding choice wines, the late application of copper salts as a protection against mildew should be avoided as much as possible.—*Comptes Rendus*, Vol. cx., No. 9.

* *Berichte Deutsch. Chem. Gesell.*, vol. xi., p. 1770; vol. xiv., p. 868; vol. xxi., p. 1839.

† Soon after the publication of my paper on the atomic weight of aluminium, I was criticised by a writer of abstracts for the German Chemical Society on account of my use of the expression "Prout's law," amazement being indicated that I should have called the "hypothesis of Prout a law." If this writer had noticed my use of inverted commas, and still more what was said in the course of two or three pages of the paper, he would have seen that the use of the expression "Prout's law" was by no means equivalent to assuming this to be a "law of nature."

ON IODATE OF CALCIUM AS AN
ANTISEPTIC.

By W. DUNNETT SPANTON, F.R.C.S. Ed.

ATTENTION was first called to this substance as a disinfectant and antiseptic by Mr. E. Sonstadt in the year 1872; and in the following year, at this gentleman's suggestion, I used it in various ways for surgical purposes, and have used it more or less ever since. I think it well to make this statement, as I find that reference has been recently made to the use of this calcic iodate in a way which suggests that its properties have only recently been discovered, and its uses known.

In the *CHEMICAL NEWS* of April 26, 1872, will be found a paper "On the Presence of Iodate of Calcium in Sea-Water," by E. Sonstadt, in which this important inference is mentioned, "that whatever iodine sea-water contains must be in the state of iodate," "and from the results of experiments made upon the iodates, and especially upon iodate of calcium, that iodine must always be set free in sea-water wherever there is putrescent organic matter; and that while this is being oxidised at the expense of oxygen in the iodate, the freed iodine slowly re-forms iodate by the decomposition of water conjointly with that of carbonate of calcium." Mr. Sonstadt further found by direct experiment that sea-water at one time would contain all its iodine as iodate, and at another time free iodine, with scarcely a trace of iodate. Several series of experiments are related which proved, in the opinion of the author of the paper, that "it is only putrescible organic matter that is decomposed by and decomposes iodate of calcium; that this substance (the iodate) possesses in a high degree the power of preventing fungoid growths in very putrescible liquids; and that this is to be attributed largely to the unstable equilibrium of the iodate which readily oxidises matter with which it comes in contact, setting free the iodine." In a further article in the *CHEMICAL NEWS*, vol. xxv., p. 231, the author describes how sea-water taken from the mouth of a river, conveying sewage, contained its iodine in a free state, and after being kept ten days the whole of the iodine had disappeared; and iodate of calcium was present as usual in sea-water taken some miles out from shore. And in another paper on the same matter, Mr. Sonstadt calculates that sea-water contains one part of iodate of calcium in every 250,000 parts by weight. So that whatever influence it may have in tending to keep pure sea-water must be due to the presence of a very minute quantity. After these papers were published the author continued to make experiments with this salt as an antiseptic and disinfecting agent; and in the *CHEMICAL NEWS*, vol. xxviii., p. 297, in an article "On the Antiseptic and Disinfecting Power of Iodate of Calcium," the results of the experiments are described. The principal putrescible substances experimented upon were urine, albumen, fish, meat, and rain-water. "Equal quantities of fresh urine were put into two test-tubes, and to one portion a small pinch of the solid iodate was added: the specimens were placed close together." After a few days the specimen to which nothing had been added became offensive; but after the addition of a solution of 1-1000th of iodate to about one-fourth of its volume, the offensive odour disappeared, although the odour of urine remained. The specimen to which solid iodate was added never became offensive, and after several weeks could not be recognised for what it was by the smell. White of egg was treated similarly: that to which solid iodate had been added kept sweet about six months, then discoloured and smelled. The other, of course, putrefied quickly. With fish, either by sprinkling, when fresh, with iodate powder, or by immersing in iodate water (containing 0.1 per cent of iodate), it kept good in hot weather about four days.

In the case of meat, the powder only was used, and with it sprinkled over the meat could be kept fresh several days longer than without it. Putrid rain-water became

odourless and agreeable to drink twenty-four after the addition to it of one-fourth its volume of 0.1 per cent of iodate water. Then further to ascertain how much might safely be taken in this way, the author took various doses of the salt, the largest being one gramme. This caused no inconvenience beyond after taste, and a slight headache next day. But he adds: "It is in cases of fever, and such diseases as typhus and cholera, propagated by some specific organic poison, that I should expect the exhibition of iodate of calcium to be followed by marked effects."

While these investigations were being carried out I was myself working at the same subject with some of the iodate which my friend Mr. Sonstadt had given to me for the purpose. In 1872 I referred to the uses and value of the salt in an address delivered to the North Staffordshire Medical Society, after I had given it a careful trial as a dressing for wounds, and also for internal administration. The salt was then little known, and I found a difficulty in obtaining it from the chemist, who more than once sent me iodide of calcium in its stead. Fortunately for me and for the subject of my experiment, I knew the difference between them, and discovered the error before using it, for the iodide is a comparatively poisonous salt, and in small doses will produce very unpleasant effects. Of this I had been warned by my friend; and anyone intending to use iodate should make quite certain he does not get iodide instead.

My experiments confirmed to a large extent those described by Mr. Sonstadt, and I have now in my possession several of the specimens I put up seventeen years ago. One, a bottle of fresh urine, to which a small quantity of iodate of calcium was added, has now no odour except that of iodine; whereas the fellow specimen without the iodate is, of course, putrid. Another, containing some boiled meat, is quite devoid of any odour of putridity; its fellow is intolerable. About the same period a patient brought to me a specimen of a lumbricus in water, and to this I added a few grains of iodate and put it aside. After a time it became almost the colour of iodine water; then would become clear again, become dark again, and it is now clear, smelling strongly, and only of iodine. The worm is more or less disintegrated, but the fluid is clear, and has never at any time had the slightest putrid smell.

One curious property the salt has, is that of retaining urine clear when added to it while fresh. Acting upon this knowledge, I employed it in some cases of chronic cystitis, in which the urine was very offensive, with excellent effect, when used for washing out the bladder. And given internally in these cases, it had the effect of clearing the urine and greatly diminishing the *fœtor*, though I found boracic acid on the whole more efficient, and have generally used it on that account.

As a dressing for wounds of all kinds, for recent amputations and injuries, as well as for suppurating or sloughing wounds, it certainly is useful as an antiseptic. But my experience of it in these cases led me to the conclusion that its insolubility (requiring about 400 parts of water for solution) was a drawback, as that strength is not enough to produce a sufficiently prolonged effect upon the discharges to keep them aseptic. And although one could use the powder itself, suspended or powdered on, I think its action is too slow for its full effect to be realised. I find in some notes I published nine years ago of excision of the tongue, a solution was found to have an excellent effect as a wash for the mouth, and four days after operation no *fœtor* could be observed in the breath (*Lancet*, 1881, vol. i., p. 911). Given internally, I was never able to convince myself that it had any marked effect, except in cases such as I have referred to, where there was cystitis or a superabundance of lithates in the urine. It occurred to me that its marked effect upon the condition of the urine might render it useful for uric acid calculus, and I gave it in some cases of renal calculus with this view. I am not able, however, to say that any well-

marked effect was observable. Knowing the action of lithium on the uric acid diathesis, it might be found that if an iodate of lithium is procurable, it might prove an active and useful drug for this affection.

So far as my experience has gone, I found the insolubility and the slowness of its action the chief drawbacks to the utility of iodate of calcium as a surgical application; but its innocuous and unirritating properties, and its marked effect upon the renal secretion, indicate a special advantage in its use for such cases as cystitis, nephritic abscess, and for renal operations generally. So many of our best antiseptics are poisonous, or irritate, or stain, that it is useful to have one such as this which is free from those drawbacks. It has at least the merit of being inodorous and almost tasteless, and of not disguising other odours by a still worse one of its own.—*The Provincial Medical Journal*.

NOTICES OF BOOKS.

Some Food Substitutes and Adulterants. (Annual Address of the President, Mr. EDGAR RICHARDS, delivered before the Chemical Society of Washington, January 23rd, 1890). Washington: D.C.

CANDIDLY speaking, we do not like the expression "food substitutes." If a substance is nutritious, digestible, palatable, and free from any injurious properties, let it by all means rank as a food; but let it be sold and used under its own name, and not put forward as a substitute for any formerly known article. Mr. Richards, on more mature reflection, can scarcely deny that the manufacturer and the dealer do not find it "directly contrary to their own interests" to add hurtful matter to food products. There are many injurious bodies used by the adulterator and the substituter, which, though they sap the health, do not promptly cause any marked symptoms of poisoning and are detected perhaps very slowly, perhaps not at all. The list appended by the author, compiled, it is said, from the Reports of the State Boards of Health, the Reports of the British Local Government Board, and those of the Paris Municipal Laboratory, by no means supports Mr. Richards in his contention that "the great majority of substances used for food adulterants or substitutes consist of cheap and harmless substances which are not injurious to health." In this list we find salts of copper, metallic poisons, Prussian blue, alum, mineral acids, antiseptics, gypsum, artificial colouring-matters, poisonous pigments, &c.; in short, a very respectable minority.

The author, further, admits that though a substance, *eg.*, water, may not be, *per se*, injurious to health, yet if introduced into, say, milk, to the exclusion, in part, of its natural and more nutritious constituents, it may be harmful, or even fatal.

No qualified and competent authority contends that oleomargarine, properly prepared, is hurtful to the consumer. The only feature to be complained of was its sale as butter, or under such delusive names as "butterine." It is worthy of note that the trade feel themselves no little aggrieved that they are now compelled to sell this substance under its own name.

Glucose, or starch-sugar, as prepared from maize in the United States, can have no injurious properties, at least if the acid used in saccharification is free from arsenic. Concerning the glucose manufactured on the Continent from refuse potatoes, we are much less confident. The potato whiskey of Germany is notoriously rich in fusel, and we fear that some substances especially prone to fermentation to generate the higher alcohols must accompany the glucose.

We do not see any chemical objection to the use of cotton oil in food, whether alone or in admixture with

other oils or fats. There is one point which, not belonging to the medical profession, we cannot presume to decide, *i.e.*, will it, being a drying oil, be as easily assimilated as the non-drying olive oil? In any case, it should be sold under its own name.

The author is not mistaken in asserting that on the European Continent the legislation concerning the adulteration of food is much superior to the English Act. There are in the former fewer loopholes for the escape of offenders. "Under the Continental laws every dealer is responsible for the quality of his merchandise; every food material must be sold under its true name; artificial products imitating a natural product must be labelled in a conspicuous and legible manner; all unwholesome foods are confiscated and destroyed without compensation to the owner; and adulterations generally are considered acts of fraud." Some of these points are found in the English law, though not all. In the fearfully mistaken law allowing coffee to be sold mixed with chicory the proportion of the latter should have been stated, and it should have been made impossible to escape by mendaciously calling the mixture "coffee as in France," or "French coffee."

Mr. Richards is not sanguine as to the suppression of adulteration in America. Public opinion is not sufficiently enlightened on this question, no more than it is in Britain.

The Practical Use of the Spectroscope. By J. PARRY, F.C.S.

THE author, in the introductory portion of his treatise, regrets that the spectroscope "has not yet found a permanent place in the laboratory of the ordinary practical chemist." For this neglect he gives several reasons, one of which is that "the instrument has hitherto been mainly in the hands of the physicist." Further, the instruments supplied for ordinary uses are unsuitable, and the directions given in the usual text-books say little of the manipulation of the instrument and of the flame or spark.

All this is perfectly true, but the greatest obstacle to the general use of the spectroscope—other than the absorption instrument—is not formally stated, though it may be inferred from the instructions here given. It lies in the necessary source of light. The Bunsen and the air blowpipe do not give a sufficiently high temperature for the volatilisation of most metals. The oxy-hydrogen blowpipe is justly pronounced very troublesome, though useful in certain special cases. But for general work, Mr. Parry prefers the electric spark derived from a powerful induction coil giving not less than a 6-inch spark. Then, to supply the needful electricity, he prefers a small dynamo driven by a gas-engine. Here, then, is the reason why the ordinary chemist does not make more general use of flame or spark spectroscopy. The expense and the space required for these instruments are the obstacle to the rapid and general extension of spectroscopy.

The author quotes very full and clear directions for adjusting the Hilger spectroscope, the type of instrument which he prefers. Bunsen's one-prism instrument he finds deficient in dispersive power. It is remarked that in Browning's six-prism instrument the adjustment is automatic. The use of photography for recording and checking spectroscopic observations is strongly insisted on. The illustrative diagrams, all of which have appeared in *Industries*, are numerous, and will prove very useful.

Separate chapters treat of the spectra of vapours at different temperatures, the spectrum of iron at varying temperatures, and the spectrum of iron heated *in vacuo*. Absorption spectroscopy does not apparently fall within the author's plan. He evidently inclines towards the theory put forward in Lockyer's "Studies in Spectrum Analysis" that the so-called elements are in reality compound bodies which, under certain conditions, may be

split. We hope and believe that Mr. Parry's work will contribute to that most desirable end, the more extended use of the spectroscope.

The Elements of Laboratory Work: a Course of Natural Science. By A. G. EARL, M.A., F.C.S. London: Longmans, Green, and Co.

THE author of this treatise has in view work in a laboratory not devoted to chemistry mainly or alone, nor to physics, but to all departments of inorganic science. His views on scientific training are very satisfactory. Thus, he concludes his preface with the expression of a hope that the course "may give some training in that habit of directly appealing to nature rather than to theories, which is the root of all scientific progress, though unfortunately it is not always made the basis of scientific education, partly from want of time, and partly from want of appliances." We must here remark that the want of time is mainly due to its profligate expenditure upon subjects of greatly less value.

The cautions on purity of the substances addressed to beginners in chemistry are greatly needed. Says Mr. Earl:—"Nothing can be more misleading than those descriptions of chemical changes which omit to state that the reacting substances are not pure and which convey the impression that chemical changes are simple enough to be amply described by an equation. They are often seriously inaccurate in themselves, and conduce to a feeling of certainty when the training of observation has barely commenced. Keenness and faculty of research is thus suppressed, when the aim of even the most elementary work should be to encourage it." A teacher who writes thus may be taken as a trustworthy guide.

The work does not bristle with mathematical formulæ, which with some writers on physical subjects are made not a means, but an end, as if a builder should erect a stately palace not for its own sake but for that of the ladders and scaffolds employed in its construction, and should leave the latter standing.

We notice the occurrence of one novel technical term, "stress," which the author uses as equivalent to "mutual action." He says that "the return of a body to the earth gives rise to the statement that it is caused by the attraction of the earth, or gravitation, but it is more exact to say that a mutual action or a stress exists between the two. If a new term was needed—of which we are not sure—Mr. Earl has done well in proposing one of English origin. The term "weight" is uniformly discarded in favour of "mass." Thus the author speaks of "atomic masses" of the elements of chemistry.

In discussing the theory of the ether, the author admits that new conceptions as to what is truly elementary matter have been gained from spectroscopic investigations. Any discussion on the nature of the supposed simple bodies would, of course, have been out of place in an elementary treatise like the present.

The chief defect which we observe is the lack of an index. But it may be warmly recommended for use in public schools and colleges.

The Trichologists' Pharmacopœia: being a Description of the Drugs used in Diseases of the Hair. By THOMAS GURNEY, M.D. (?), L.R.C.P., L.R.C.S., Physician to the Hair Hospital, &c. London: Osborne, Garrett, and Co.

To outsiders, like ourselves—non-trichologists—it is a novelty to see the extent of this novel pharmacopœia. In the work itself we see some very satisfactory passages mixed up with occasional errors. Thus, it is going too far to say that vinegar is a liquid "of a brown colour," and that it is "prepared from malt." The brown colour is an accidental feature, often produced artificially, and abundance of vinegar is prepared from other materials.

Acidum boracicum is explained as being "bone acid." This, we think, must be a clerical error: there is no boracic acid present in the bones of animals. An interesting remark is that the use of this acid in preserving milk is decidedly pernicious. "Its addition to milk is a very common source of skin eruptions." This the author concludes from his own observations.

Hydrocyanic acid is mentioned as being applied to kill parasites in the head, with the proviso that it "must be used very carefully!"

The following remark is curious:—"In certain localities in England water exists in liquid, solid, and gaseous states." Sea-water is declared very injurious to the hair, which after a sea bath should always be washed in not less than a gallon of pure water.

Oil of cajeput is said to be imported "from Bavaria and Singapore." We presume Batavia is meant.

The frequent references to syphilitic ulcerations, warts, &c., on the head are sufficiently alarming, and might lead our ethicists to question whether some of their recent movements have not been a mistake.

We are told that a "watery solution of cochineal allowed to stand in a warm spot will develop the *coccus cacti*." Is this an assertion of abiogenesis?

The following is too true:—"Truly in medicine, as in politics, fads are set up and grasped by the ignorant as principles. Miles of speeches are made and written about fads, often in themselves ludicrous, and principles are forgotten!"

We are told that "one part of the cyanide (potassium), two of plaster of Paris, and two and a half of water stirred together and poured, whilst liquid, into a wide-mouthed bottle forms a hard floor, which is constantly giving off a poisonous vapour, which vapour will kill insects without injuring their plumage or structure." The vapour certainly kills many insects, but there are others which it does not affect in the least.

Mr. Gurney is very severe on the soap trade, holding that "money making is more considered in the preparation of soaps than the effect they have on complexions." The author's views on the manufacture of soap are somewhat antiquated. "The usual way of manufacturing common soap," he tells us, "is to boil some low priced oil with the lye of wood ashes." This process would, of course, yield a soft soap only, but the lye of wood ashes has been now laid aside in favour of the pure potash from Stassfurt.

The author gives throughout his work many cautions as to the random and indiscreet use of various agents. In no department is quackery more rampant than in the treatment of the hair, and if he can depose or discredit it he will have performed a good work.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 9, March 10, 1890.

Thermic Researches on the Allotropic States of Arsenic.—MM. Berthelot and Engel.—The author's observations show that the two varieties of arsenic develop almost identical quantities of heat on forming one and the same combination. The difference is even too slight to be guaranteed with certainty.

The Absorption of Atmospheric Ammonia by Vegetable Soil.—H. Schloesing.—Calcareous soils, air-dried, are able to absorb as much as 108 m.grms. of ammoniacal nitrogen per kilo. It is probable that a part of the ammonia absorbed forms, with certain organic matters, compounds stable enough not to reproduce am-

monia under the treatment employed. The author's experiments show that bare vegetable soil, calcareous, acid or neutral, dry or moist, absorbs atmospheric ammonia in important quantities.

Nomination.—The Academy proceeded to nominate a Correspondent for the Physical Section, *vice* Prof. Kirchhoff, deceased. Lord Rayleigh obtained 42 out of 45 possible votes, and was proclaimed elected.

Combination of Hydrogen Phosphide and of Ammonia with Boron Chloride and Silicon Sesquichloride.—A. Besson.—Boron chloride combines directly with hydrogen phosphide at temperatures below + 20°, forming a white solid unstable in the air and instantly decomposable by water. The author assigns to this compound the formula BCl_3PH_3 . Dry ammoniacal gas at +8° expels the hydrogen phosphide from this compound, 4 vols. of ammoniacal gas taking the place of 1 vol. PH_3 . The new compound is $2BCl_3 \cdot 9NH_3$. Silicon sesquichloride combines directly with dry gaseous ammonia, forming a white solid, $Si_2Cl_3 \cdot 5NH_3$. The reaction of hydrogen phosphide with silicon sesquichloride is not interesting.

Compounds of the Alkaline Metals with Ammonia. J. Moutier.—A thermo-chemical explanation of the formation of the compounds described by M. Joannis.

Determination of the Free Halogens and of Iodides in Presence of Chlorine and Bromine.—P. Lebeau.—(See p. 163).

Formation of Lead Hyposulphite.—J. Fogh.—The author calculates the formation-heat of this compound at +76 cal.

Researches on the Application of the Measure of Rotatory Power to the Determination of the Compounds resulting from the Action of Malic Acid upon the Neutral Lithium and Magnesium Molybdates.—D. Gernez.—Experiments upon solutions of levo-rotatory malic acid mixed with gradually increasing quantities of sodium molybdate show, in solutions of similar volume, the formation of successive compounds resulting from the union of 1 equiv. malic acid with quantities of the salt corresponding to 1, 2, 3, 5 equivalents, the production of which is characterised by the manner in which the rotatory power of the solutions varies and the maximum values through which it passes.

Volumetric Determination of Tannin.—E. Guenez.—This memoir will be inserted in full.

Determination of Acetone in Methylic Alcohol and in the "Methylenes" of Denaturation.—Leo Vignon.—The method of Kramer is applicable to the determination of very small quantities of acetone in methylic alcohol, but not to its determination in the "methylenes of denaturation," *i.e.*, methylated spirit.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., February, 1890.

Manufacture of Alkali.—B. Hasenclever (*Chem. Industrie*).—Zinc blende is now successfully used in various establishments in Germany for the manufacture of sulphuric acid and liquid sulphurous acid. The author fears that if the Chance process is adopted by all the manufacturers of Leblanc soda the price of sulphur will be seriously reduced.

Chemical Studies on the Ammonia-Soda Process.—H. Schreiber (*Chem. Industrie*).—The author estimates that whilst on the original ammonia-process 200 kilos. of salt were required to produce 100 kilos. sodium carbonate, the recent improvements will reduce this quantity to 115 to 120 kilos.

Historical Notice of Lavoisier.—M. Berthelot.—In this interesting survey the author quotes some of the sayings of the men who overthrew the Academy of Sciences and proscribed Lavoisier. Jean Bon St. André

said that the republic was under no obligation to make *savants* or to bestow upon them any privilege. Bouquier exclaimed in the Convention against the existence of a caste of egotistic and speculative *savants*. Every superiority, even if intellectual, was proclaimed an aristocracy, and as therefore to be suppressed. M. Berthelot remarks that this menacing language in our own time still echoes in the daily press. Guyton de Morveau, Monge, and especially Fourcroy, are blamed for not having even attempted to save Lavoisier. Fourcroy, if he did not, as it has been asserted, intrigue against Lavoisier, made himself very conspicuous in the suppression, or, as it was called, the purification of the "Lycée des Arts."

Metallurgical Review—This section contains notices on the part played by sulphur in the processes employed in the extraction of zinc, on the hygroscopic property of certain colamines of inferior quality, on a peculiarity of blende in roasting, and on the manufacture of aluminium. These papers are taken from the *Chemiker Zeitung* and the *Zeit. für angewandte Chemie*.

The Action of Water at High Temperatures and at great Pressures upon Wood and Cellulose.—H. Tauss (*Dingler*).—Pure cellulose gives traces of sugar at the ordinary pressure. At higher pressures the quantity of sugar increases, but at 20 atmospheres it is converted into hydrocellulose. Wood is attacked by water at the ordinary pressure, but the action reaches its maximum at 5 atmospheres, when beech wood loses 26.7 per cent of its weight, of which 11 per cent become sugar. There are also produced dextrins, precipitable by alcohol. No vanilline is obtained from the aqueous or ethereal extracts, or from the dried residues. The colour-reactions of lhl must be due to the transformation of lignine into carbohydrates.

MISCELLANEOUS.

Filtering-Paper from Grycksbo, Sweden.—In his "Treatise on Chemistry," vol. viii., p. 222, Berzelius expresses himself regarding the valuable qualities of this paper as follows:—"The best filtering-paper I know of comes from Grycksbo, in Dalecarlia; the water with which it is made is so pure that it does not give any reaction indicating the presence of foreign substances, nor does it retain any of the earths in solution. The acid and the water extract from this paper and the ash which it leaves when burnt are not more abundant nor of any other nature than those which come from the most unadulterated linen; that is to say, they do not amount to more than 0.006 of its weight. Latterly they have begun to make this paper an article of export, and assuredly there are few localities where nature has combined with so many favourable circumstances as at Grycksbo for the fabrication of an excellent filtering-paper." Fresenius's "Guide to Quantitative Chemical Analysis" (1862, 5th Edit., p. 81), on the subject of filtering-paper, says:—"The best is that known by the name of 'The Swedish Filtering-Paper,' and which bears the water-mark of J. H. Munktel."'

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Celluloid.—Can any of the scientific readers of your journal give me the formula of a suitable celluloid solvent? If so, I shall feel obliged.—CELLULOID.

Sugar in Carrots.—Will some correspondent be good enough to inform me the percentage of saccharine matter to be found in a carrot, and also if any of our ordinary vegetables (excepting beet) contain more?—A. S.

MEETINGS FOR THE WEEK.

TUESDAY, 8th.—Royal Medical and Chirurgical, 8.30.
Photographic, 8.
WEDNESDAY, 9th.—Microscopical, 8.
Pharmaceutical, 8.
THURSDAY, 10th.—Institute of Electrical Engineers, 8.
FRIDAY, 11th.—Astronomical, 8.
Quekett Club, 8.

TO CORRESPONDENTS.

Torbay.—It would be impossible to answer your questions intelligibly without giving a paper on the subject. You should consult some good work on Volumetric Analysis—Sutton's, for instance.

THE LONDON HOSPITAL MEDICAL COLLEGE. THE SUMMER SESSION will COMMENCE on THURSDAY, May 1st.

The Hospital, which is the largest general hospital in the kingdom, contains nearly 800 beds, all in constant use. There are wards for accidents, surgical and medical cases, diseases of women and children, and ophthalmic cases. Special departments for diseases of the eye, ear, throat, skin, and teeth, and for cancer, tumours, diseases of the bladder, piles, and fistula. Number of in-patients last year, 8873; out-patients, 101,548; accidents, 7456.

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N.B. Special arrangements have been made to meet the requirements of the Examining Board in England so as to enable Students entering in May to pass Part I. (Chemistry and Chemical Physics), and Part II. (Materia Medica and Pharmacy) of the First Examination in July.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1585.

NOTE ON MANURE DRYERS.

By VINCENT EDWARDS, F.C.S.

THIS being the busy time at manure works, a few words in connection with the above may be of interest. It is of course necessary to add to some manures substances which will not only increase bulk, but at the same time absorb moisture. I have come to the conclusion that there is a good deal of danger of serious error in this matter; in fact, of undoing what has been done at so much expense by adding "dryers" containing iron and alumina; in fact, some manufacturers may be deluded by unscrupulous dealers, as it is almost certain that many of these stuffs are worthless. I have made some experiments with ashes from furnaces, and find that some contain large quantities of iron, which, notwithstanding any new ideas to the contrary, is a very dangerous ingredient to supply without discrimination to plants. It is true that some may be benefited by the use of iron as a manure, but the advantages of its general use are more than doubtful. Manufacturers should see that all substances used for dryers are nearly free from iron. No superphosphate or bone manure should contain more than 0.7 per cent of iron (Fe), which is poison to the plant and injury to the manure.

Dublin, March 28, 1890.

PROFESSOR GRÜNWALD'S MATHEMATICAL SPECTRAL ANALYSIS.

(Continued from p. 159).

DR. KAYSER, when criticising the groups of rays of magnesium, reproaches the author for having included in the third group (embracing the hydrogen rays of magnesium, i.e., those belonging to the primary substance "b" in that chemical condition in which it also occurs in free hydrogen = b_4), the sharp margins of the bands which Liveing and Dewar have observed in the flame spectrum of magnesium burning in the free air, as he is of opinion that these bands belong, not to magnesium, but to a compound which it may form with hydrogen. But in the demonstration that these margins at 3865, 3860, &c., in the ultra violet (the wave-lengths of which were placed together in a separate column) correspond to the hydrogen rays of magnesium (third group), there lies an important discovery of the writer's, which he has scarcely brought into sufficient prominence, and for which he surely should not receive blame. When magnesium burns in the free air it combines not only with the oxygen of the atmosphere, but it withdraws oxygen from the omnipresent watery vapour and sets the hydrogen at liberty. The latter, in its nascent state, reacts upon the rest of the magnesium vapour, strengthening and rendering visible a portion of the magnesium bands otherwise invisible. This fact is not altered even by assuming that the action of the liberated hydrogen leads to the formation of a magnesium hydride. The latter can have at most the formula MgH_2 , since MgH_2 could not exist in the magnesium flame. But the compound MgH , as a combination of gaseous components in equal volumes, emits only rays belonging in part to free magnesium, in part to free hydrogen, and in part to both in common, the intensities of which are chiefly different from the intensities which they possess in the free components. Entire series of rays which in the latter

are too faint to be noticed become perceptible in the compound MgH , and inversely.

As to the bands, totally distinct from the above, which Liveing and Dewar are really inclined to refer to $Mg + H$, namely (5618-5576 . . .) (5566-5525) (5513, 5512, 5511-5458 . . .) (5210-5185) (see *Proc. Roy. Soc.* 1881, p. 196), the author has only examined them closely after his publication on magnesium and carbon, and finds that their luminous maxima as given by Liveing and Dewar belong to the first or helium group of the magnesium rays. Hence it follows that at least a part of these bands (emitted by magnesium in presence of hydrogen in the electric spark under a pressure of several atmospheres) belong to the group mentioned. Here is another "discovery" hitherto not published, but communicated to Prof. Liveing on September 14th and 20th, 1887, which will, he trusts, survive the criticism of Dr. Kayser.

As to the further wave-lengths criticised by Dr. Kayser, it must be remarked that, according to the researches of Liveing and Dewar (*CHEM. NEWS*, 1881, vol. xliii, pp. 261-263, 271-273), magnesium emits rays which are otherwise not observed, but which, nevertheless, like the above-mentioned bands (or luminous maxima of bands), belong to magnesium, and can be without difficulty introduced into the corresponding groups of rays. Their wave-lengths were obtained from the above source, as also from the "Investigations on the Spectrum of Magnesia" (*Proc. Royal Soc.*, vol. xxxii., 189, 203). Thus, λ 4808 was observed by Liveing and Dewar in the blue as a faint line in the electric spark, 4481 strong in the electric spark in presence of hydrogen, but not in the arc; 4350 in the arc-spectrum only; 4586 in the spark spectrum; 4703 in both; 4165, in place of 4166, is a clerical error, since 4166 agrees better with the criteria. That the respectively adjacent wave-lengths, 3330 of Liveing and Dewar, and 3329.1 of Hartley and Adeney (Abney?), are drawn together in the conspectus on page 11 of the memoir on magnesium and carbon is an oversight. In the tables they are kept distinct.

Finally, it must be mentioned that the author obtained a series of wave-lengths (which were not to be found in the original memoirs then at his disposal) from a well-known compilation, the "Text-book of Spectral Analysis," by Dr. Kayser (1883), with the unfortunate result that several of the numbers given, e.g., 4456, 4705, 3896, and 3894, are inaccurate! The author has learnt the sparing trustworthiness of the numerical data of this manual on obtaining from England and Ireland the original treatises and the "Reports of the British Association." Dr. Kayser's work should be used with great caution by those who have not all the original documents at command.

The correct values of the two last-mentioned wave-lengths, 3895 and 3893 (instead of 3896 and 3894), as well as the wave-lengths of various other magnesium lines, were re-determined by Liveing and Dewar, in 1888 (*Proc. Royal Soc.*, vol. xliiv.), and, of course, could not be utilised in 1887.

I call attention to the fact that if a rhythmic relation exists between two wave-lengths λ and λ' of the spectrum, or of two different spectra, this relation may be recognised and deduced even from rather defective measurements. For if $\lambda + \delta$ and $\lambda' + \delta'$ are two faulty values of the true wave-lengths—

$$\lambda \text{ and } \lambda' \text{ and } \frac{\lambda'}{\lambda} = \frac{m}{p},$$

where m and p represent whole numbers, the error of—

$$\frac{\lambda' + \delta'}{\lambda + \delta} - \frac{\lambda'}{\lambda} = \frac{\lambda' \delta' - \lambda \delta}{\lambda^2} = \frac{m}{p} \left\{ \frac{\delta'}{\lambda'} - \frac{\delta}{\lambda} \right\}$$

is very small, especially when λ and λ' are considerable. This is the cause why the Balmer's rhythmic relations among a portion of the hydrogen lines (which belong to the primary element a of $H = ba_4$) may be deduced even from Angström's measurements. Further, the mere

accidental character of a rhythmic relation among a large number of the corresponding wave-lengths of the two spectra is much less probable than it would be the case with a constant but non-rational relation.

The author, therefore, did not scruple three to four years ago to attempt the verification of his theory, and in connection therewith to search for any existing rhythmic relations between two groups of lines of different spectra. This was done, notwithstanding the then very incomplete and, in some cases, rather faulty data. Along with the more recent determinations by Liveing and Dewar, Hartley and Adeney (Abney?), Thalén and Cornu, he utilised the former results of such men as Kirchhoff, Plücker, Huggins, H. W. and W. C. Vogel, especially when more later measurements were wanting.

It should never be forgotten that Rowland's new method of measuring wave-lengths by means of concave gratings, which admits of a degree of accuracy previously unknown, has found entrance into England and the rest of Europe only within the last few years. The increased precision thus attained will be to the advantage of the author's theory and of the comparisons which it requires. At present there is especial need of new accurate measurements of the lines of oxygen and of the luminous maxima of its bands, both alone and under the influence of the aqueous vapour of the oxyhydrogen flame. The collocation of different data compelled by external circumstances has led J. S. Ames (*Amer. Chem. Journ.*, 1889, vol. x., p. 138) to a supposed fundamental objection to the theory. The wave-lengths 6742 (Kirchhoff) and 6740 (Huggins) are two distinct data, in consequence of errors of observations, for one and the same cadmium line which in the author's spectral analysis of cadmium appear mentioned in the first group of the cadmium rays, the former (Kirchhoff's) being in especial type to signify that it displays all the criteria of the group in a particularly satisfactory manner. Ames assumes that, according to the author's theory, two lines should be present, though one only is visible, and, in common with Dr. Kayser, he sees here a fundamental objection to the theory! Here it must be remarked that even if accidentally both wave-lengths should fulfil all the criteria of the first group (which is here not the case), it would merely follow that both must belong to the same form of condensation of the primary element "c," but not necessarily the actual equal visibility of the corresponding rays in the spectra of all substances which contain "c" in this form of condensation, because its intensity is variously modified by the influence of the other constituents of such substances which may intensify the ray in one and in another enfeeble it down to disappearance. These and similar criticisms are not valid against the author's theory.

(To be continued).

EXAMPLES OF "SOLUTION COMPOUNDS."*

By G. GORE, LL.D., F.R.S.

THE term "solution compounds" has been applied chiefly to those substances which exist only whilst dissolved in water, &c., and are decomposed on evaporating or crystallising the liquids. A method of detecting those bodies and of ascertaining the combining proportions of their ingredients by means of the "voltaic balance" has already been published (see *Roy. Soc. Proc.*, vol. xlv., p. 265).

The formula of each "solution compound" in the following series of examples is the one yielding the smallest amount of voltaic energy, and is indicated by a star (*). The act of chemical union is usually attended by a great loss of such energy, and the relative amount of

voltaic energy of the new compound is usually very much smaller than that of the mean of its constituents. Each "solution compound" is recognised by a depression of such energy. In each of the following cases only a sufficient number of measurements are given to show a portion of the depression of energy caused by chemical union of the ingredients of the compound. One example only is given of each class of compounds, and only average amounts of available voltaic energy are stated; the proportions of such energy given do not include the amounts lost by "local action." Zinc platinum couples and aqueous solutions were employed in all cases.

EXAMPLES.

1.—Element with Element.

Chemical equivalents.		Average energy.
4Br+5Cl	at 20° C.	1,934.496
4" +4" *	"	1,817.901
4" +3"	"	1,981.035

2.—Element with Monobasic Acid.

4HCl+5Cl	at 21° C.	863.774
4" +4" *	"	739.922
5" +4"	"	876.300

3.—Element with Bibasic Acid.

2H ₂ SO ₄ +5I	at 18° C.	320.460
2" +4I*	"	267.958
2" +3I	"	312.815

4.—Element with Tribasic Acid.

Citric acid+4Br	at 20° C.	775.944
" +3" *	"	636.956
" +2"	"	706.506

5.—Element with Tetrabasic Acid.

H ₄ P ₂ O ₇ +5Br	at 20° C.	716.768
" +4" *	"	586.785
" +3"	"	614.269

6.—Element with Monobasic Salt.

4AmCl+5Br	at 17° C.	355.698
4" +4" *	"	308.699
3" +4"	"	326.081

7.—Element with Bibasic Salt.

2K ₂ SO ₄ +5Cl	at 20° C.	74.368
2" +4" *	"	50.648
2" +3"	"	54.536

8.—Element with Tribasic Salt.

2Na ₂ HPO ₄ +7I	at 21° C.	30.869
2" +6I*	"	26.556
2" +5I	"	28.703

9.—Element with Tetrabasic Salt.

Na ₄ P ₂ O ₇ +5Br	at 21° C.	104.387
" +4" *	"	82.289
" +3"	"	86.377

10.—Monobasic Acid with Monobasic Acid.

4HF+5HCl	at 19° C.	162.078
4" +4" *	"	151.760
4" +3"	"	170.678

11.—Monobasic Acid with Bibasic Acid.

2H ₂ CrO ₄ +5HCl	at 17° C.	72.445
2" +4" *	"	62.056
2" +3"	"	68.746

12.—Monobasic Acid with Tribasic Acid.

Citric acid+4HF	at 20° C.	107.223
" +3" *	"	102.319
" +2"	"	107.223

13.—Monobasic Acid with Tetrabasic Acid.

H ₄ P ₂ O ₇ +5HNO ₃	at 20° C.	26.795
" +4" *	"	23.731
" +3"	"	25.969

* Read before the Birmingham Philosophical Society, Nov. 12, 1889.

14.—Bibasic Acid with Bibasic Acid.		30.—Tribasic Acid with Tetrabasic Salt.	
Chemical equivalents.	Average energy.	Chemical equivalents.	Average energy.
3Oxalic Acid + 4H ₂ SO ₄ at 20° C.	81,232	3(KCr ₂ SO ₄) + 5Citric Acid .. at 23° C.	25,969
4 " + 4 " "	63,851	3 " + 4 " "	24,035
5 " + 4 " "	78,304	3 " + 3 " "	25,559
15.—Bibasic Acid with Tribasic Acid.		31.—Tetrabasic Acid with Monobasic Salt.	
2Citric Acid + 4H ₂ CrO ₄ at 18° C.	924,835	5KNO ₃ + H ₄ P ₂ O ₇ at 28° C.	2,726
2 " + 3 " "	779,734	4 " + " "	2,253
2 " + 2 " "	927,682	3 " + " "	2,659
16.—Bibasic Acid with Tetrabasic Acid.		32.—Tetrabasic Acid with Bibasic Salt.	
2H ₄ P ₂ O ₇ + 5H ₂ SO ₄ at 20° C.	25,587	5Na ₂ SO ₄ + 2H ₄ P ₂ O ₇ at 25° C.	1,755
2 " + 4 " "	21,648	4 " + 2 " "	1,577
2 " + 3 " "	23,542	3 " + 2 " "	1,841
17.—Tribasic Acid with Tribasic Acid.		33.—Tetrabasic Acid with Tribasic Salt.	
5Citric Acid + 4H ₃ PO ₄ at 25° C.	3,900	5Na ₂ HPO ₄ + 3H ₄ P ₂ O ₇ at 21° C.	936
4 " + 4 " "	3,495	4 " + 3 " "	842
3 " + 4 " "	3,823	3 " + 3 " "	962
18.—Tribasic Acid with Tetrabasic Acid.		34.—Tetrabasic Acid with Tetrabasic Salt.	
3H ₄ P ₂ O ₇ + 5Citric Acid at 20° C.	13,119	5Na ₄ P ₂ O ₇ + 4H ₄ P ₂ O ₇ at 21° C.	171
3 " + 4 " "	11,637	4 " + 4 " "	136
3 " + 3 " "	13,231	3 " + 4 " "	165
19.—Monobasic Acid with Monobasic Salt.		35.—Monobasic Salt with Monobasic Salt.	
4KCl + 5HF at 17° C.	12,241	4KNO ₃ + 5KCl at 15° C.	275
4 " + 4 " "	11,063	4 " + 4 " "	211
4 " + 3 " "	12,241	4 " + 3 " "	259
20.—Monobasic Acid with Bibasic Salt.		36.—Monobasic Salt with Bibasic Salt.	
2Na ₂ SO ₄ + 5HNO ₃ at 18° C.	86,377	2(Ba ₂ NO ₃) + 5NaCl at 15° C.	61'4
2 " + 4 " "	77,446	2 " + 4 " "	54'3
2 " + 3 " "	88,480	2 " + 3 " "	61'4
21.—Monobasic Acid with Tribasic Salt.		37.—Monobasic Salt with Tribasic Salt.†	
Na ₂ HPO ₄ + 4HCl at 19° C.	78,754	2LCl + Na ₂ HPO ₄ at 13° C.	-1,390
" + 3 " "	70,959	3 " + " "	-1,558
" + 2 " "	81,805	4 " + " "	-1,295
22.—Monobasic Acid with Tetrabasic Salt.		38.—Monobasic Salt with Tetrabasic Salt.	
Na ₄ P ₂ O ₇ + 5HCl at 18° C.	8,637	Na ₄ P ₂ O ₇ + 5KCl at 16° C.	-7,657
" + 4 " "	8,123	" + 4 " "	-9,623
" + 3 " "	8,880	" + 3 " "	-7,951
23.—Bibasic Acid with Monobasic Salt.		39.—Bibasic Salt with Bibasic Salt.	
5KCl + 2H ₂ SO ₄ at 15° C.	10,765	4Na ₂ CO ₃ + 5K ₂ Cr ₂ O ₇ at 17° C.	-23,785
4 " + 2 " "	9,867	4 " + 4 " "	-28,574
3 " + 2 " "	11,637	4 " + 3 " "	-26,615
24.—Bibasic Acid with Bibasic Salt.		40.—Bibasic Salt with Tribasic Salt.	
4K ₂ SO ₄ + 5H ₂ CrO ₄ at 18° C.	52,438	4Na ₂ SO ₄ + 3Na ₂ HPO ₄ at 20° C.	779
4 " + 4 " "	41,413	3 " + 2 " "	727
4 " + 3 " "	46,049	2 " + 3 " "	818
25.—Bibasic Acid with Tribasic Salt.		41.—Bibasic Salt with Tetrabasic Salt.	
4Na ₂ HPO ₄ + 7H ₂ SO ₄ at 21° C.	37,706	5Am ₂ SO ₄ + 2Na ₄ P ₂ O ₇ at 25° C.	-1,134
4 " + 6 " "	30,931	4 " + 2 " "	-1,346
4 " + 5 " "	33,215	3 " + 2 " "	-1,163
25.—Bibasic Acid with Tetrabasic Salt.		42.—Tribasic Salt with Tribasic Salt.	
2Na ₄ P ₂ O ₇ + 5H ₂ SO ₄ at 21° C.	14,004	4Na Citrate + 5Na ₂ HPO ₄ at 22° C.	381
2 " + 4 " "	12,145	4 " + 4 " "	365
2 " + 3 " "	13,008	4 " + 3 " "	400
27.—Tribasic Acid with Monobasic Salt.		43.—Tribasic Salt with Tetrabasic Salt.	
4NaCl + Citric Acid at 18° C.	10,526	5Na ₂ HPO ₄ + 3Na ₄ P ₂ O ₇ at 21° C.	-1,715
3 " + " "	8,707	4 " + 3 " "	-1,894
2 " + " "	8,912	3 " + 3 " "	-1,723
28.—Tribasic Acid with Bibasic Salt.		44.—Tetrabasic Salt with Tetrabasic Salt.	
7BaBr ₂ + 4Citric Acid at 21° C.	2,172	5Am ₄ P ₂ O ₇ + 4Na ₄ P ₂ O ₇ at 23° C.	-351
6 " + 4 " "	2,044	4 " + 4 " "	-379
5 " + 4 " "	2,324	3 " + 4 " "	-337
29.—Tribasic Acid with Tibasic Salt.		45.—Sugar + Common Salt.	
3Na ₂ HPO ₄ + 4Citric Acid at 19° C.	4,330	2Cane sugar + 5NaCl at 11° C.	-43'6
4 " + 4 " "	3,900	2 " + 4 " "	-47
5 " + 4 " "	4,461	2 " + 3 " "	-44'5

† The loss of voltaic energy in this case and several others is indicated by a maximum minus number, instead of a minimum plus one.

It is evident in all these cases, from the proportions of substances required to reduce the energy to the smallest number, that the two uniting substances must be chemically equivalent to each other.

The foregoing series of examples show that all kinds of soluble elements, acids, acid, neutral, and alkaline salts, &c., whilst in aqueous solution together, unite with each other indiscriminately in the definite proportions by weight of their ordinary chemical equivalents.

As in every one of these cases, either one of the two ingredients may be replaced by almost any other soluble ingredient of equal chemical value, and as each of these instances is only a solitary example of a large number of the same class of compounds, and each compound is capable of uniting with nearly every other compound individually whilst in solution, and these more complex ones are similarly capable of uniting with others of equal chemical value almost without limit, except in cases where separation by precipitation or evolution of gas occurs (see *Roy. Soc. Proc.*, vol. xlv., p. 266; also "Loss of Voltaic Energy by Chemical Union," *Proc. Birm. Phil. Soc.*, 1888, vol. vi., Part 2), it is evident that the total number of possible "solution-compounds" is exceedingly great—certainly thousands.

The fact, which has been so largely disclosed by means of the voltaic balance, that all kinds of chemical substances, when in mutual solution, unite with each other indiscriminately and irrespective of the chemical nature of the substances, has an important bearing upon chemical action, and throws great light upon the cause of chemical union.

The following are the average amounts of available voltaic energy of the ingredients employed in making the above compounds, and from these numbers and the foregoing ones the amounts of loss of such energy which occurred during the formation of the compounds can be ascertained:—

	Degrees Centigrade.	Average voltaic energy.
Cl.. .. .	at 11	1,282,000,000
Br	13.7	81,022,500
HCl	16.5	9,344,092
H ₂ SO ₄	19	3,900,941
I	13.5	3,310,985
HNO ₃	19	3,204,395
H ₂ CrO ₄	18	1,611,111
HF	18	1,151,363
KCl	8	697,803
NaCl	15	207,589
Citric acid	22	36,597
KCr ₂ SO ₄	19	35,902
H ₃ PO ₄	26	34,952
H ₄ P ₂ O ₇	17	20,336
AmCl	13.5	15,069
KNO ₃	20	10,841
Oxalic acid	15	9,450
K ₂ Cr ₂ O ₇	13	7,156
Am ₂ SO ₄	20	2,634
K ₂ SO ₄	12	2,274
Na ₂ HPO ₄	15	2,057
Na ₂ SO ₄	13	2,020
Na Citrate	22	1,466
Am ₄ P ₂ O ₇ (variable) ..	23	327
LCI	16	204
Water	16	0
Cane sugar	15	-67.8
Ba ₂ NO ₃	19	-163
BaBr ₂	17	-163
Na ₄ P ₂ O ₇	18	-232
Na ₂ CO ₃	19	-14,795

The amounts of voltaic energy with zinc-platinum couples of more than three hundred "solution-compounds" are given in a paper on "Relative Amounts of available Voltaic Energy of Aqueous Solutions" (*Ibid.*, 1889, vol. vii., Part 1).

EXAMINATION OF CORPSES FOR ALKALOIDS AND OTHER NITROGENOUS BASES.*

DR. ANTON SEYDA.

THE examination of the organs of a corpse for alkaloids is one of the most difficult chemical problems, as every chemist will admit, the more distinctly the longer experience he has had in this sphere. Our fragmentary knowledge of the ptomaines and of the conditions in which they are formed and again disappear, involves much uncertainty of judgment on the alkaloidal nature of a substance. So much has been already written on ptomaconiines, ptomastrychnines, &c., that we could not wonder if a publication were to appear "On a Strychnine or Morphine obtained from Putrid Albumen."

It has been rightly said:—"A nitrogenous base obtained from a corpse can only be pronounced identical with a well-known vegetable alkaloid when the two agree together physically, chemically, and physiologically. In this case the confusion of a ptomaine with an alkaloid is almost out of the question. On the other hand, in such a position of things it cannot be denied that a really existing vegetable alkaloid may easily be overlooked, especially if we consider that we have to do with only very small quantities. In reading the accounts of ptomaines the author has not been able to avoid a suspicion that the chemist concerned had been almost too cautious, and on the faith of a few not very decided reactions has been induced to pronounce in favour of the presence of ptomaines.

In the present state of science it is, under certain circumstances, easier to prove the presence of a ptomaine than of a vegetable or artificial alkaloid. To consider the proof of the absence of an alkaloid or of the presence of a ptomaine in amorphous residues, as furnished on the faith of doubtful or defaulting colour-reactions, is an equally hazardous affair, as when the solution of a residue gives with the general reagents for alkaloids a more or less intensely coloured precipitation, or none at all. The physical, chemical, and physiological behaviour of the alkaloids in a pure state is tolerably known, but not in an impure state, or better, in a not quite pure state, and such occur for the most part in the examination of the organs of a corpse.

Extracts from such organs are best obtained by treatment with tartaric alcohol. The fat separated along with the water requires no further treatment. It is not, indeed, absolutely impossible that it may act as a solvent for some organic poison, e.g., nitroglycerin. For isolating and determining this poison in matter free from fat the author recommends the following method:—The air-dry substance is shaken out with chloroform and from the filtrate the chloroform is chiefly distilled off in a retort, the residue is then cautiously evaporated in a moderately warm water-bath in a beaker glass previously tared, dried over concentrated sulphuric acid, and then weighed again.

If the fat is saponified and the soap is dissolved in water and shaken up with ether, the latter is covered intensely yellow; on evaporation there is obtained a yellowish crystalline residue, insoluble in water, which may be obtained pure by repeated crystallisation, and proves to be cholesterol.

The extracts obtained from the stomach are mostly light yellow; the colour being more intense in cases when the bile has poured out into the stomach. Extracts of a more dark brown colour are obtained from the large abdominal glands which are filled with blood, and this colour passes more or less strongly into all the liquids which have been obtained by shaking out the residues. This evil can be decreased by freeing the organs as far as possible from blood.

The solutions of the extracts may often be cleared in

* *Chemiker Zeitung.*

the following manner:—To the alcoholic solution an alcoholic solution of tartaric acid is added as long as a precipitate is formed (the substance obtained being always tested for the presence of an alkaloid); it is filtered off and drained, the filtrate is evaporated, the residue is taken up in water, the filtered clear solution is neutralised with potassa, concentrated, and mixed with alcohol. The potassium tartrate is thus separated out, and carries down with it a part of the colouring-matter. The watery solutions of the extracts finally resulting (an absolutely neutral solution cannot be obtained in any case, so that both red and blue litmus-paper remain unaffected, hence the solutions must be set so that blue litmus-paper is very slightly reddened) and they are then tested with the general reagents for alkaloids; more or less decided precipitates are obtained in most cases.

Before proceeding to a closer examination, the liquids should always be tested for their behaviour with iodic acid and also for the presence of meconic acid. A reduction of iodic acid will often occur (the acidulation must be effected with tartaric acid and not with hydrochloric acid, since an excess of this latter may decompose the iodic acid), and is not always due to morphine. Occasionally this reducing substance is met with in the ethereal extract obtained from an acid solution. Sometimes it cannot be detected after extraction either in the amyl or in any other of the residues from extraction, nor, remarkable to say, the original watery extract. This substance seems to be decomposed by the supersaturation with potassa-lye or the treatment with the different solvents.

If iodic acid is not reduced, the specific search for morphine becomes unnecessary.

(To be continued).

ON THE SYNTHESIS OF FUMARIC ACID.*

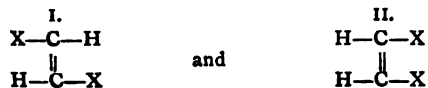
By E. H. KEISER.

(PRELIMINARY COMMUNICATION).

VAN'T HOFF† has proposed the following stereometric formulæ for fumaric and maleic acids:—



Johannes Wislicenus‡ has shown in a series of important papers that it is possible to determine experimentally the stereometric formulæ of certain isomeric compounds. A consideration of the hypothesis put forward by him, suggested the idea that it ought to be possible to prepare both fumaric and maleic acids synthetically from acetylene. In accordance with Van't Hoff and Wislicenus's theory, the di-halogen additive compounds of acetylene can exist in two isomeric forms having the formulæ:—

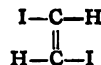


in which X represents any halogen atom. And, further, compounds having the constitution represented by formula I. are more stable than those having the structure represented by the second formula. Fumaric acid would then appear to be closely related to the halogen derivatives of the first class, and maleic acid to those of the second.

It occurred to me that it might, perhaps, be of interest in this connection to start with acetylene, and prepare, in the first place, two isomeric di-halogen additive compounds, and then endeavour to transform these into fumaric and maleic acid. The investigation is not yet completed, but one of the acids, namely, fumaric acid, has been prepared in this way from acetylene.

Acetylene was prepared by the action of alcoholic potash upon ethylene bromide, and the purified gas was passed through a series of wash-bottles containing crystals of iodine covered with a layer of absolute alcohol. After a time, the iodine disappeared, and from the liquid two isomeric acetylene di-iodides were separated. One of these compounds is a solid at ordinary temperatures; the other is a liquid. The solid di-iodide is much more stable than the liquid variety. It does not decompose on standing, and can be sublimed without suffering change. On the other hand, the liquid di-iodide undergoes decomposition when heated, and cannot be distilled with steam without being decomposed. These compounds have been prepared by Sabanejeff,* who has analysed them and found them to have the composition represented by the formula $\text{C}_2\text{H}_2\text{I}_2$. No attempt was made by him to determine their constitution.

In accordance with the Van't Hoff hypothesis, the solid acetylene di-iodide, which is much more stable than the liquid di-iodide would have the constitution represented by the formula—



and would, therefore, belong to the same general class of acetylene derivatives to which fumaric acid belongs. Now, experiment shows that this solid acetylene di-iodide can be transformed into fumaric acid.

Nine grms. of the acetylene di-iodide crystals (m.p. 73°) were dissolved in alcohol, and 5 grms. (two molecules) of potassium cyanide added, and the solution was boiled for thirty-six hours in a flask with an inverted condenser. Caustic potash was thereupon added, and the boiling continued for two hours longer. On cooling the contents of the flask, a considerable quantity of needle-shaped crystals separated from the liquid. They were removed from the solution, and on examination proved to be the potassium salt of fumaric acid, which crystallises in the form of needles, insoluble in cold alcohol. More of the salt was obtained from the mother-liquor. The aqueous solution of the potassium salt was treated with silver nitrate, and a white precipitate consisting of the silver salt was obtained. The silver salt was purified by dissolving it in nitric acid and re-precipitating it by carefully neutralising the solution with ammonia. The silver salt of fumaric acid is characterised by its great insolubility in water, and by the fact that when it is heated it deflagrates like gunpowder. Both of these properties were exhibited by the silver salt of the acid made by synthesis.

A quantitative determination of the percentage of silver gave the following result:—

0.2039 grm. of the salt, dried at 100°, gave
0.1786 grm. of AgCl = 65.97 per cent Ag.

	Calculated for $\text{Ag}_2\text{C}_4\text{H}_2\text{O}_4$.	Found.
Ag..	65.43	65.97

The free acid itself was recognised by its insolubility in water; it was precipitated from moderately concentrated solutions of its salt by the addition of strong acids. It will be analysed as soon as larger quantities of it have been obtained in pure condition.

In 1882, Sabanejeff‡ studied the action of potassium cyanide upon acetylene di-bromide and obtained an acid

* Read at the Meeting of the Chemical Section of the Franklin Institute, February 20, 1890.

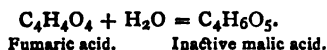
† "Laerung der Atome im Raume," p. 21.

‡ "Räumliche Anordnung der Atome in organischen Molekülen," Ann. Chem. (Liebig), cccvi., 53.

* Ann. Chem. (Liebig), clxxviii., 118.

† Ann. Chem. (Liebig), cccvi., 275.

having the formula $C_4H_6O_5$. It is probable that fumaric or maleic acid was first formed in his experiments, which afterwards, by the prolonged action of boiling caustic alkali, was converted into the acid $C_4H_6O_5$. It has been shown by Linnemann and Loyd¹ that when fumaric acid is heated with caustic alkalis, it is gradually changed into an inactive malic acid, thus:—



A more detailed study of the reactions, which give rise to the formation of the two acetylene di-iodides, as well as the attempt to prepare maleic acid from acetylene, is reserved for future work.

THE SPONTANEOUS IGNITION OF COAL CARGOES.†

By Professor VIVIAN B. LEWES,

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FIFTEEN years ago the loss of life and property caused by the spontaneous ignition of coal cargoes became so serious that the Board of Trade, acting in unison with the Committee of Lloyd's, urged upon the Government the necessity for appointing a Royal Commission to inquire into and report upon the possibility of preventing a class of disaster as appalling in nature as it is destructive in result. The Commission, which was appointed in April, 1875, had the good fortune to be aided in their inquiry by the scientific knowledge of Dr. Percy and Mr., now Sir Frederick, Abel, and after collecting and collating all the evidence which could be obtained, they, in the following year, published their report upon the subject. In this report much valuable evidence is passed in review, and much sound advice is given for the guidance of those employed in the shipment of coals; but whether it is that the sight of a blue-book scares the ordinary reader, or that the circulation of such literature, often of the most valuable character, is of necessity very limited, the fact remains that the conditions at present existing are as nearly bad as they were before the publication of the report.

In the nine years immediately following the report, viz., 1875 to 1883, 57 coal-laden vessels are known to have been lost from spontaneous ignition of their cargoes, whilst during the same period 328 were missing from unknown causes, a large percentage of these losses being undoubtedly due to the same cause; and these, again, form but a very small percentage of the cases in which cargoes have heated and fired, but in which the vessel has been saved; and now, within the last few years, the statement has gained ground that with the general increase of temperature in steam-ships, due to the introduction of triple expansion engines and high-pressure boilers, spontaneous firing in the coal-bunkers and coal cargoes is very much increased, and that many accidents arise from this cause.

Under these circumstances, Mr. Martell suggested to me some time ago that an inquiry into the causes and possible prevention of this very serious evil would be work, not only likely to be acceptable to the members of this Institute, but also one that was needed in the Service, as well as in the mercantile marine; and I have now much pleasure in bringing before you the results obtained in a long series of experiments, and which, taken in conjunction with the work done by others on the subject, throws a somewhat clearer light upon the causes of this particular class of phenomenon, and enables suggestions to be made for its prevention.

Coal is a substance of purely vegetable origin, formed out of contact with air by long exposure to heat and pressure, from the woody fibre and resinous constituents of a monster vegetation which flourished long before the earth was inhabited by man: and coal may therefore be looked upon as a form of charcoal which, having been formed at a temperature lower than that of the charcoal burner's heap and under great pressure, is very dense, and still retains a quantity of those constituents, which, in the latter case, are driven off, as tar, wood naphtha, &c.; and these bodies consist essentially of compounds containing carbon and hydrogen, together with a little oxygen and nitrogen, and form the volatile matter and hydrocarbons of the coal.

Besides the carbon and hydrocarbons, coal also contains certain mineral bodies which were mostly present in the sap and fibre of the original vegetation, and which give the ash which is left behind when the coal is burnt.

These substances consist chiefly of sulphate of lime or gypsum, silica, and alumina, whilst in nearly all kinds of coal is to be found a substance called disulphide of iron, coal brasses, or pyrites, which has been formed by the gradual reduction of the sulphates by carbonaceous matter in the presence of iron salts, and which, during the combustion of the coal, is decomposed, giving off sulphur compounds, and leaving behind oxide of iron, which gives the reddish brown colour to the ash left by many kinds of coal.

Of these constituents of coal, the only ones which play no part in the phenomena attending heating and spontaneous ignition are the mineral constituents other than the pyrites, and we have therefore to deal with the chemical actions which take place when the carbon, hydrocarbons, and brasses contained in newly-won coal come in contact with air and moisture.

(a) The Influence of Carbon in Producing Heating.

Carbon is one of those substances which possess to an extraordinary degree the power of attracting and condensing gases upon their surface, this power varying with the state of division and density of the particular form of carbon used. The charcoal obtained from dense forms of wood, such as box, exhibit this property to a high degree, one cubic inch of such charcoal absorbing*—

Ammonia gas..	90	cubic inches.
Sulphuretted hydrogen..	55	"
Carbon dioxide ..	35	"
Ethylene (olefiant gas)..	35	"
Oxygen ..	9.25	"
Nitrogen ..	6.5	"

whilst certain kinds of coal also exhibit the same power, although to a less degree.

The absorptive power of newly-won coal due to this surface attraction varies, but the least absorbent will take up $1\frac{1}{2}$ times its own volume of oxygen, whilst in some coals more than three times their volume of the gas is absorbed. This absorption is very rapid at first, but gradually decreases, and is, moreover, influenced very much by temperature, for reasons which will be explained later.

The absorption is at first purely mechanical, and itself causes a rise of temperature, which, in the case of charcoal formed in closed retorts, as in preparing alder, willow, and logwood charcoal for powder-making, would produce spontaneous ignition if it were not placed in sealed cooling vessels for some days before exposure to air.

The rate of absorption varies with the amount of surface exposed, and therefore able to take part in this condensing action, so that when coal or charcoal is finely powdered, the exposed surface being much greater, absorption becomes more rapid, and rise of temperature at once takes place. If charcoal is kept for a day after it

* *Ann. Chem.* (Liebig), cxviii., 80.

† Read at the Thirty-first Session of the Institution of Naval Architects, March 28, 1890; the Earl of Ravensworth in the Chair.

* Sausure.

has been made, out of contact with air, and is then ground down into a powder, it will frequently fire after exposure to the air for thirty-eight hours; whilst a heap of charcoal powder, of 100 bushels or more, will always ignite. It is for this reason that, in making the charcoal for powder, it is always kept, after burning, for three or four days in air-tight cylinders before picking over, and ten days to a fortnight before it is ground.

In the case of coal, this rise in temperature all tends to increase the rate of the action which is going on; but is rarely sufficient to bring about spontaneous ignition, as only about one-third the amount of oxygen being absorbed by coal that is taken up by charcoal, and the action being much slower, tends to prevent the temperature reaching the high ignition-point of the coal. Air-dry coal absorbs oxygen more quickly than wet coal.

(b). *The Action of the Bituminous Constituents of the Coal in Spontaneous Ignition.*

All coal contains a certain percentage of hydrogen, which is in combination with some of the carbon, and also with the nitrogen and oxygen, and forms with them the volatile matter in the coal, and the amount present in this condition varies very largely, being very small in anthracite and very great in cannel and shale. When the carbon of the coal absorbs oxygen, the compressed gas becomes very chemically active, and very soon commences to combine with the carbon and hydrogen of the bituminous portions, converting them into carbon, dioxide, and water vapour. This chemical activity increases rapidly with rise of temperature, so that the heat generated by the absorption of the oxygen causes it to rapidly enter into chemical combination. Chemical combination of this kind—i.e., oxidation—is always accompanied by evolution of heat, and this further rise of temperature again increases rapidity of oxidation, so that a steady rise of temperature is set up, and this taking place in the centre of a heap of small coal, which, from the air and other gases enclosed in its interstices, is an admirable non-conductor of heat, will often cause such heating of the mass, that if air can percolate slowly into the heap in sufficient quantity to supply the necessary percentage of oxygen for the continuance of the action, the igniting-point of the coal would be soon reached.

The effect of rise of temperature in increasing the rapidity of chemical actions of this kind can be realised from the effect which it has in the spontaneous ignition of oily waste or rag.

If a substance like cotton-waste be rendered oily with anything except the mineral oils, it acquires the power of taking up oxygen from the air, and this oxidising the oil gives rise to heat. At ordinary temperatures this oxidation is slow, and, consequently, it may be days before the rise in temperature becomes sensible, but when this point is reached the oxidation proceeds with remarkable rapidity, and in a few hours the point of ignition is reached and the mass bursts into flame, whilst if the oily waste be placed in a warm place at first, spontaneous ignition is only a question of hours, or sometimes even minutes.

Galletley found that oily cotton at ordinary temperatures took some days to heat and ignite, whilst placed in a chamber warmed to 130° to 170° F. (54° to 76° C.), the cotton greasy with boiled linseed ignited in one hour fifteen minutes, and olive oil on cotton in five hours, and in a chamber heated to 180° to 200° F. (82° to 93° C.) olive oil on cotton ignited in two hours.

It has been suggested that very bituminous coal, such as cannel, shale, and coals containing schist, is liable to spontaneous ignition from the fact that a rise in temperature would cause heavy oils to exude from them, which, by undergoing oxidation, might cause rapid heating. But experiment not only shows that this is not the case, but that the heavy mineral oils have a remarkable influence in retarding heating, cotton waste, oily with easily oxidisable

oils mixed with 20 per cent of heavy mineral oil, being exempt from heating.

(c). *The Action of Iron Disulphide, Pyrites, or Coal Brasses in Promoting Spontaneous Ignition.*

Ever since Berzelius first expressed the opinion that the heat given out by the oxidation of iron disulphide into sulphates of iron might have an important bearing on the heating and ignition of coal, it has been adopted as the popular explanation of that phenomenon; and although the work of Dr. Richters clearly proves this not to be the case, the old explanation is still given, a notable exception, however, being in the case of our great metallurgist, Dr. Percy, who, as early as 1864, pointed out that probably oxidation of the coal had also something to do with spontaneous combustion, a prediction amply verified by Dr. Richters' researches some six years later.

This disulphide of iron is found in coal in several different forms, sometimes as a dark powder distributed throughout the mass of the coal, and scarcely to be distinguished from coal itself. In larger quantities it is often found forming thin golden-looking layers in the cleavage of the coal, whilst it sometimes occurs as large masses and veins, often an inch to two inches in thickness, but inasmuch as these masses of pyrites are very heavy, they rarely find their way into the screened coal for shipment, many hundreds of tons of these "brasses" being annually picked out from the coal at the pit's mouth, and utilised in various manufacturing processes. If the air is dry the pyrites undergo but little change at ordinary temperatures; but in moist air they rapidly oxidise when in a finely-divided condition, the first action being the formation of ferrous sulphate and sulphur dioxide, together with the liberation of sulphur, the relative amounts of the two latter being regulated by the temperature and the supply of air, whilst longer contact with moist air converts the ferrous sulphate into a basic ferric sulphate generally termed "misy."

It is during this process of oxidation that the heat supposed to cause the ignition is evolved. But when it is considered that some of the coals most prone to spontaneous combustion contain only eight-tenths of a per cent of iron pyrites, and rarely more than 1½ per cent, the absurdity of imagining this to be the only cause of ignition becomes manifest. If 100 lbs. of coal were taken, and the whole of the pyrites in it concentrated in one spot and rapidly oxidised to sulphate, the temperature would barely be raised to 100° C., if all loss of heat could be avoided. Besides which, in certain manufactures pure iron pyrites are largely used, and, when free from carbonaceous matter, may be kept in a state approaching to powder in heaps containing many hundred tons; and although undergoing continual oxidation, I have been unable to trace a single case of heating, much less a rise of temperature which would approach the igniting-point of coal. When, however, it is mixed with finely-divided carbonaceous matter, then heating and ignition is a frequent occurrence in even moderate sized heaps.

I have carefully determined the igniting-point of various kinds of coal, and find that—

Cannel coal	ignites at 698° F. = 370° C.
Hartlepool coal	" 766 = 408
Lignite	" 842 = 450
Welsh steam coal	" 870.5 = 477

So that no stretch of imagination could endow the small trace of pyrites scattered through a large mass of coal, and undergoing slow oxidation, with the power of reaching the needful temperature.

Dr. Richters fully realises this point, and discards the idea of the pyrites doing anything more than adding their mite to the causes which bring about rise of temperature. In this, however, I think he is mistaken, my experiments, which will be published when complete, pointing to the fact that they may increase the liability to ignition when

present in large quantities, and do so by liberating sulphur under certain conditions. Now, sulphur has an igniting-point of 482°F . or 250°C ., so that the presence of free sulphur would lower the ignition-point of the coal by considerably over 100 degrees Centigrade, the sulphur in this case playing exactly the same part that it does in gunpowder, in which it lowers the point of ignition, and increases the rapidity of combustion. A still more important part played by the pyrites is that as they become oxidised to ferrous sulphate they swell in size, and so tend to split up the coal into small pieces, and by exposing a large extent of fresh surface to the air cause increase of temperature and energetic chemical action.

We can now trace the actions which cumulate in ignition. The newly-won coal is brought to the mouth of the pit, and at once commences by virtue of its surface action to absorb oxygen from the air, but unless piled in unusually large heaps, and a good deal broken, it does not, as a rule, show signs of heating, as the exposed surface is comparatively small, and the air finding its way freely between the lumps keeps down the temperature. The coal is now screened, and the obtrusively large lumps of brasses picked out; it is then put in the trucks and enjoys the disintegrating processes of joltings and shuntings innumerable, every jar adding to the percentage of small coal present, and a corresponding increase in the size of the surface exposed to the air. Arrived at the docks, it has to be transferred from the truck to the ship, which is done by one of the numerous forms of tips, shoots, or spouts employed for the purpose, and it is during this operation that more harm is done than at any other period. The coal first shot into the vessel by reason of the distance which it has to fall is broken down into small lumps, and having to bear the impact of the succeeding load falling upon it from a height, rapidly becomes powdered into slack, whilst the succeeding loads falling in on the cone so formed get more or less broken down, so that by the time the cargo is all taken in, a dense mass of small coal is to be found under the hatchway, and it is invariably at this point that heating takes place, as the large surface exposed fresh to the air by the breaking down of the coal causes rapid absorption of oxygen, and consequent rise of temperature. This sets up chemical combination between the oxygen absorbed by the coal and the hydrocarbons and coal brasses.

The combination of the brasses with oxygen causes the swelling of the oxidised mass and splitting up of the coal; fresh surfaces are exposed, and more absorption of oxygen takes place, and the igniting-point of the sulphur vapour and sulphur compounds distilled out of the pyrites is reached, and rapidly raises the temperature to the ignition-point of the coal. It is only in cases where large quantities of dense coal brasses are present that this action can take place, as in the ordinary case, where 1 or 2 per cent only of pyrites are present, the sulphur vapour distilled out from the pyrites is oxidised to sulphur dioxide at temperatures far below the point of ignition of sulphur vapour; and in such cases the heat of absorption and oxidation of the bituminous portions of the coal is amply sufficient to raise the temperature to the requisite 752° to 932°F . (400° to 500°C .).

(To be continued).

Action of Sulphuric Acid upon Aluminium.—A. Ditte.—Cold dilute sulphuric acid seems to have no action upon aluminium, yet, as the formation of aluminium hydroxide evolves 195.8 calories, this metal should at ordinary temperatures decompose water and *a fortiori* dilute acids. The author in this paper demonstrates that such is the case, and that if a plate of aluminium immersed in dilute sulphuric acid seems not to be attacked, the cause is that it becomes coated with a continuous layer of hydrogen which prevents all direct contact with the liquid.—*Comptes Rendus*, cx., No. 11.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

ON the 27th ultimo, the first Anniversary Dinner of the Chemical Society took place at the Hôtel Métropole, under the presidency of Dr. W. J. Russell, F.R.S. About 150 sat down to dinner, including the President of the Royal Society, the President of the Pharmaceutical Society, the President of the Society of Chemical Industry, the President of the Institute of Chemistry, the President of the Physical Society, the President of the Institute of Civil Engineers, the President of the Society of Electrical Engineers, the Director of the Royal Gardens (Kew), the Master of the Drapers' Company, Sir F. A. Abel, Sir H. Roscoe, Sir F. Bramwell, Sir Owen Roberts, Dr. M. Foster, Dr. H. Müller, Dr. J. H. Gladstone, Mr. A. H. Allen, Mr. W. Anderson, Dr. H. E. Armstrong, Dr. E. Atkinson, Dr. Atfield, Mr. W. Roberts-Austen, Mr. H. Bauerman, Mr. H. Bassett, Mr. F. W. Bayley, Mr. W. P. Beale, Mr. M. Bechler, Mr. W. J. Bell, Mr. E. Best, Mr. E. J. Bevan, Mr. B. Blount, Mr. E. R. Blundstone, Dr. H. Borns, Mr. P. Braham, Mr. B. Brough, Dr. L. Brunton, Mr. J. Y. Buchanan, Mr. A. Carpmal, Mr. A. Cooper, Mr. W. Crookes, Mr. C. F. Cross, Mr. R. H. Davies, Prof. J. Dewar, Mr. W. H. Dixon, Mr. F. Down, Mr. W. R. Dunstan, Mr. C. Ekin, Mr. T. Fairley, Prof. G. C. Foster, Mr. W. Foster, Mr. G. B. Francis, Dr. J. H. Gilbert, Mr. M. C. Godson, Mr. J. G. Gordon, Mr. Friese Green, Mr. A. J. Greenaway, Mr. C. E. Groves, Mr. R. Harrison, Dr. G. Harley, Mr. E. S. Harris, Mr. C. W. Heaton, Mr. W. Hills, Herr V. Hofmann, Dr. J. Hopkinson, Mr. D. Howard, Mr. W. L. Howie, Prof. J. J. Hummel, Dr. W. Ince, Dr. F. R. Japp, Prof. Judd, Dr. W. Kellner, Mr. T. A. Lawson, Mr. J. B. Lyon, Mr. G. H. Makins, Mr. Edward Matthey, Mr. B. McNeil, Mr. G. Mellin, Dr. Mers, Dr. G. Moody, Mr. E. R. Moritz, Mr. F. Moul, Mr. W. Naylor, Mr. W. Newton, Prof. W. Odling, Mr. J. F. Page, Mr. P. R. Parsons, Dr. B. Paul, Dr. W. H. Perkins, Mr. S. U. Pickering, Mr. J. J. Pilley, Mr. M. Prentice, Mr. W. Prideaux, Dr. A. Pullar, Mr. R. D. Pullar, Mr. L. O. M. Pyke, Prof. W. Ramsay, Prof. E. Reynolds, Dr. Ruhemann, Mr. A. G. Salamon, Mr. J. H. Selson, Dr. Senier, Mr. H. R. Smith, Mr. F. Smith, Mr. A. Smithells, Mr. C. W. Stewart, Dr. L. Thorne, Mr. W. Thorp, Prof. T. E. Thorpe, Mr. J. M. Thomson, Dr. Tidy, Dr. W. A. Tilden, Mr. C. Tookey, Mr. E. W. Voelcker, Mr. R. Warrington, Rev. Henry White, Mr. W. M. Williams, Mr. W. P. Wynne.

After the usual loyal toasts, the President, Dr. W. J. RUSSELL proposed "Prosperity to the Chemical Society," in the following words:—

I am afraid that some may think that the Chemical Society is becoming frivolous as it grows old, for to-day it arrives at the mature age of forty-nine, and for the first time gives a party on its birthday. Before I ask you to toast it on this festive occasion, let me say a few words concerning its birth and early history. For the moment, I stand as a sort of father to the Society, and to-day allow me to use a father's right of telling what a wonderful child it has been even from its birth, and how strong and active it is at the present time. My remarks shall not, however, extend to such a length as parents' remarks sometimes do when speaking of favourite children.

On the 23rd of February, 1841, some twenty-five or so chemists, who had been summoned by Mr. Warrington, met at the rooms of the Society of Arts to consider whether it was desirable to found a Chemical Society. They seem all to have been of one mind, and unanimously to have declared that it was advisable to found such a society. Three, I believe, of those present at this preliminary meeting are still with us. They are Sir W. Grove, Sir L. Playfair, and Mr. Heisch. The

provisional committee then formed suggest an outline of what they think should be the constitution of the Society, and on the 30th of March of the same year a general meeting is held, the Society is definitely founded, Thomas Graham is elected President, and Sir W. Grove a member of Council.

The Society seems at its formation to have numbered some 77 members, and of these original members six are still upon our list. The reading and discussion of papers, and the publishing of a journal seems at once to have followed the formation of the Society, and the work done by the Fellows of our Society in those early days is recorded in the three volumes of *Memoirs and Abstracts of the Chemical Society*. These appeared in small parts and at very irregular intervals.

If we might measure the age of our Society, not by years, but by the changes which it has seen in the science which it represents, and the progress which it has registered, then it becomes a Society of high antiquity.

On glancing through these three volumes of *Memoirs*, one is struck not only by the simplicity of the facts and formulae there described, but above all by the immense development of our science since that time.

It seems to take one back to a very primitive time when we find recorded in the first of these volumes, that Dr. Clark exhibited to the Society his method of ascertaining quantitatively the comparative hardness of water by means of a tincture of soap, and promises further details at a future meeting. In the same volume Fownes describes how CO can best be prepared from ferrocyanide of potassium, and Mr. Croft, it is stated, on April 19, 1842, exhibited and described Dr. Bunsen's new galvanic arrangement. The original work done by the Fellows in those days has stood well, and in criticising their work we must remember how inferior the tools they had to work with were to those at our command.

In addition to the original papers in these early volumes are translations in full or abstracts of foreign papers; thus, from the first, was begun a practice which has been so successfully carried on till the present day. Our past president, Dr. Gilbert, translates for the first volume of these *Memoirs* a long paper by Redtenbacher and Liebig, on the atomic weight of carbon, and we find also in this volume Bunsen's paper on the "Radical of the Cacodyl Series," and we find Will and Varentz describing and defending the accuracy of their soda-line process.

In the second volume is an important paper by Drs. Muspratt and Hofmann, describing the preparation of aniline from nitro-benzene, and shortly afterwards these same chemists describe a new base; it is called toluidine. In the same volume are also important papers by Joule and Playfair on atomic weights and specific gravities, and one by R. Hunt, interesting as showing how different and distinct light, heat, and chemical force were supposed at that time to be.

Volume three proclaims the discovery of gun-cotton, and Teschemacher and Porrett, and afterwards Gladstone, examine its composition.

These three volumes carry the history of the Society to the end of 1847. The Society now numbers between 200 and 300 members, and they, it appears, were no longer satisfied with a journal which appeared only at irregular and often long intervals, and determined to replace it at the end of this year by a quarterly journal. Great stress was laid when this form of journal was established on its containing not only original papers, but also carefully drawn up abstracts of important chemical papers published in other journals, a practice which has, with so much advantage, been continued to the present day, but in addition to the abstract was appended to each annual volume what it would trouble us at the present day to furnish a list of, all the chemical papers published during the year in British and foreign journals. In the volume for 1848 this list occupies nineteen pages.

The establishment of this Quarterly Journal gave life and vigour to the Society, and chemistry was now being most vigorously studied on the Continent. Giessen was at the height of its fame, and the influence of Liebig was being strongly felt, even in this country. Laboratories were being founded, and in the Anniversary Address of the President, in 1847, he announces the establishment in London of three chemical laboratories designed to further the prosecution of original research; one, the College of Chemistry, and the two others at the older colleges of the University of London.

This first volume of the *Quarterly Journal* is full of matter which has kept its interest to the present day. I am not going to give you even an epitome of its contents, but we are all happy to see here the joint author of two of the papers which it contains, Sir F. Abel. He, in conjunction with Prof. Rowney, give very elaborate and careful analyses of the Trafalgar Square water and the Cheltenham mineral waters. Among the many good papers in this volume there is one other I cannot pass over without mentioning; it is the one by Mansfield "On Coal-Tar," a paper which, on account of its own intrinsic merits, would have a lasting importance, but, as indicating clearly the scientific and practical value of coal-tar, which till then had been looked upon as an objectionable article, is of special and remarkable interest. The simple way in which he describes "some of the useful properties of benzole" is like reading a novel of the last century, only much more interesting, or reading an account of a body described as new which one had looked upon as having existed from the earliest times.

This volume also records the fact that Hofmann had begun to work upon the organic bases. I do not intend, you will be glad to hear, even rapidly going through the remaining five and forty volumes of our *Journal*, but I think there is an interest at the present moment in briefly noting what was being done when our Society was first formed.

The beneficial influence which our Society has exercised in the bringing together of people of like tastes and pursuits no doubt has been great, but the publication of its *Journal* has probably done most towards extending a knowledge of chemical science.

In 1847 the original memoirs had to give way to the *Quarterly Journal*, and thirteen years later the *Quarterly Journal* has to give way to a monthly *Journal*, for the fellows again clamour for the more rapid publication of their papers. A graphic history of the *Journal* is given by Dr. Hofmann in his Presidential Address in 1862, when the *Monthly Journal* was established. He says that after "the year 1860 it was found convenient to discontinue the alphabetical list of the heads of chemical papers. In fact this list, which, when first published, occupied not more than 19 or 20 pages, had gradually expanded beyond legitimate proportions, filling, in the last volume, 79 pages, or one-fourth of the whole volume. By its discontinuance a considerable amount of additional space was thus given for original communications and for abstracts, but it proved inadequate for the requirements of the Society, and consequently, he goes on to say, the *Monthly Journal* was established, and he concludes by adding these words, which time has shown to be true to the letter:—"The rank a Society holds will always depend upon the number, value, and rapidity of its publications. I believe, therefore, that the transition from a *Quarterly* to a *Monthly Journal* will be received with general approbation. "Not only does this change secure to our contributors almost immediate publication, but it will enable us henceforth to publish abstracts of all valuable chemical papers which are dispersed in the *Proceedings* and *Transactions* of the several learned societies, in which they are not always easily accessible, and to make our *Journal* a sort of *Comptes Rendus* of all the work done in chemical science throughout the country.

We all must feel how wise these words were, and how at the present time we are attempting to do exactly what

Hofmann describes nearly thirty years ago, and the result is as I said this afternoon. I think no Society can boast of a Journal more complete, more useful, and more up to date than ours.

Turning for a moment from the theoretical and literary side of the development of chemistry to the practical and instrumental, the change during the last half century is not less striking nor less important. At the present time it is really difficult for us to realise how incomplete were the laboratories and how clumsy was the apparatus which was then in use. Even the refined process of organic analysis illustrates this. In 1841, Liebig had only lately described this process, which will ever be so nearly associated with his name, and which really made the analysis of organic bodies possible; compare how the process, although essentially the same, was then and now carried on. I can remember the use of charcoal for heating the tube, the use of sheet india-rubber for joining the tubes, which it did in a way which gave the greatest anxiety to the operator when he had, with a hot coal, to test the tightness of the apparatus; and how often the test gave an unsatisfactory result. Then, with regard to the use of charcoal, what an amount of fanning it did require, and what an amount of dust and ashes it did give rise to, and altogether what a hot and dirty operation it was—no laboratory at the present day would tolerate it. Now the tightness of the apparatus is easily assured, and the whole heating of the tube regulated by turning a gas-tap. Surely mechanical ingenuity and dexterity have done much to aid in the development of our science. Even the founders of our Society, men who but the other day were with us, would be astonished at the gigantic and elaborately fitted laboratories of the present day—astonished to see how electricity, gas, and steam are now forced into the service of the chemist, and how operations and experiments in general have been shortened in time and increased in accuracy.

In 1847, the President, in his Anniversary Address, calls attention, as I before mentioned, to the establishment in London of three laboratories for original research. I know not how many exist in this country at the present time, but beside the university cities, every large town has its well-equipped laboratory, and in London the number still increases; and if, among the latest additions, the large laboratories now being built by the conjoint Board of the Medical Colleges are not for strictly chemical purposes, the work carried on there, if it be real and useful, as I doubt not it will be, must to a large extent be dependent on chemical science; and of a more purely chemical character are the large research laboratories lately established by the Pharmaceutical Society.

What our Society has done in the past to aid and extend chemical science is clearly written and fully acknowledged, and the question now is what will it do in the future? The answer, I doubt not, is that it will do even more in the future for the progress of the science than it has done in the past.

Sir. F. A. ABEL then proposed "The Kindred Societies and Institutions," to which Sir GABRIEL STOKES and Sir LOWTHIAN BELL replied.

Professor MICHAEL FOSTER then proposed the health of the Visitors, which was responded to by Sir. F. BRAMWELL and Dr. THISELTON DYER.

The health of the Chairman was proposed by Sir HENRY ROSCOE, and the proceedings then terminated.

Corresponding Reactions of Carbazol and Pyrrol.

—S. C. Hooker (*Berichte Deutsch. Chem. Gesell.*) mentions that both carbazol and pyrrol give the pine-wood reaction, give a deep blue compound with isatin and sulphuric acid, both give two distinct compounds with benzoquinone, one of a violet-red, soluble in ether, and the other green, insoluble in ether. Both pyrrol and carbazol give, with picric acid, a compound which crystallises in red needles.

NOTICES OF BOOKS.

Chemical Laboratory Labels. Second Edition. Part III. Compiled by W. H. SYMONS, F.R.M.S., F.C.S., &c. London: Gallenkamp and Co.

THESE labels are clear, sufficiently large, and not encumbered with needless matter, such as formulae. The nomenclature is very "advanced," the old familiar acids have disappeared, and in their room we find such names as hydrogen chloride, hydrogen nitrate, &c. Hydrogen citrate, however, is wanting. Many of the labels, such as "test-tubes," "retorts," "retort-stand fittings," &c., are, of course, intended, not for bottles, but for drawers, presses, or the like. "Hydrogen," "oxygen," and "carbon dioxide" are destined for gas-holders. A feature of practical value is that the labels are exceedingly well-gummed.

CORRESPONDENCE.

LARD.

To the Editor of the Chemical News.

SIR,—Kindly allow me to make an addendum to my letters on the above subject. I have read Dr. Swindell's letter in your last week's issue.

In the year 1885 I found $1\frac{1}{2}$ to $2\frac{1}{2}$ per cent of water in several samples of lard. Since then I have, at times, found more. The publicity given to these examinations proved, I think, of beneficial result, inasmuch as latterly I have found the samples of the various brands of lard which I have examined almost free even of moisture. Lard, however, is melted and cooled in jacketed pans, containing steam and cold water. Should a leakage take place in the internal jacket of either, water is bound to show itself in the lard. If such leakage can be proved, and it can be shown that immediate action, upon discovery, was taken to stop it, I do not think a magistrate would be justified in inflicting a penalty for wilful adulteration. But this opens out a great field of enquiry, which I shall not enter upon. The magistrate has only to deal with the subject at issue, in this case water, and to inflict a fine to show the world that the public insist upon having dry lard. If it can be shown that it was by accident the water became incorporated with the lard, the magistrate can, of course, use his discretion as to the amount of the fine, but convict he must.

If anyone buys lard knowing that it contains cotton-seed oil, he must sell it as a compound. If he does not, Dr. Swindell and myself can only be of one opinion, viz., that his action is illegal, and, of course, must be punished, for the law must be obeyed.

With respect to the addition of other matter to lard, viz., stearin, I think Dr. Swindell's "light" is of a refractive rather than a reflective nature. I notice that he has toned down his "doctored dripping" to "peck dripping." When he writes again on lard his common sense will probably take the place of his theoretical opinion, and he will call the fat of swine, when rendered down and "larded," or improved, by stearin, "Lard," like the rest of the world.—I am, &c.,

WILLIAM BROWN.

3, Hereford Road, Seaforth,
near Liverpool, April 2, 1890.

The Camphorates of the Dextro- and Levo-Borneols.—A. Haller.—The author finds that the total etherification of camphoric acid is not effected until a relatively high temperature has been reached, and only with the anhydride. Under these conditions the production of isomers is certain. One of the functions of camphoric acid in the acid ethers approximates to that of the phenols.—*Comptes Rendus*, Vol. cx., No. 11.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 11, March 17, 1890.

Reactions between Vegetable Soil and the Atmospheric Ammonia.—M. Berthelot.—A portion of soil may be made at pleasure either to absorb almost all the ammonia contained in a given atmosphere, or to give off a part of its nitrogen in the form of ammonia. All intermediate and even contrary results may be realised by experiments systematically directed, but without being applicable, except to the special circumstances of the observation.

Researches on Phenomena produced during the Condensation of Gaseous Carbides under the Influence of the Effluve.—P. Schützenberger.—The gases studied have been carbon monoxide, cyanogen, ethylene, and acetylene. In operating upon carbon monoxide the author obtained a brown matter of the composition:—

Carbon	45.6
Hydrogen	0.6
Oxygen	53.8
	100.0

These figures would lead to a formula between $C_{12}H_2O_{10}$ and $C_{12}H_2O_{11}$. The sum of the weights of the products formed (brown solid, water, and carbon dioxide) exceeds the weight of the carbon monoxide utilised by 0.046 gm. Water and oxygen must therefore have been introduced from without, through the glass, as the author purposes demonstrating in a future memoir.

Double Lead and Sodium Hyposulphites.—J. Fogh.—The salt of Lenz, $PbS_2O_3 + 2NaS_2O_3$, is not a simple mixture, but a true double hyposulphite, probably the only one existing.

A New Crystalline Form of Ammonium Chloride.—G. Geisenheimer and F. Leteur.—The crystals in question contain about 1.5 per cent of ruthenium subchloride. They were obtained from the washing waters left on preparing pure iridium by the method of Deville and Debray.

The Monobenzoic and Dibenzoic Acetals of Sorbite.—J. Meunier.—Monobenzylsorbite has the composition $C_6H_{13}O_5(C_7H_5O)$. Dibenzylsorbite is represented by $C_6H_{12}O(C_7H_5O)_2$.

On Oxytetric Acid.—Ch. Cloez.—Not adapted for useful abridgment.

The Value of the Heat of Hydratation of Maleic Anhydride.—Iw. Ossipoff.—The hydratation-heat of maleic anhydride when forming maleic acid is 9.6 cal. If it yields fumaric acid, 11.1 cal.

Dissociation of the Hydrochlorates of Amines and of the Salts of Dissolved Fatty Acids.—J. Müller.—This dissociation can be demonstrated by means of phenolphthalein.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., February, 1890.

Fluorescent Colouring-Matters derived from Resorcline (Weselsky's Colours).—E. Noelting.—A description of the preparation and properties of resazurine (diazoresorcline) and of resorufine (diazoresorufine) with a notice of hystazarine, an isomer of alizarine. In a comparative table are given the reactions of hystazarine, ulizarine, quinizarine, xanthopurpurine, anthrarufine,

chrysazine, anthraflavic acid, metabenzene dioxanthraquinone, isoanthraflavic acid, and isochrysazine.

Fire-proof Compositions.—Tissues can be rendered unflammable at about 30 centimes per square metre, and retain this property for several months, in one experiment for three years. Wood can be still better secured if the protective salts are allowed to penetrate into its substance.

Determination of Ferrocyanides in Spent Purifying Mass.—O. Knublauch.

Analysis of Spent Purifying Mass.—C. Moldenhauer and W. Leybold.

Extraction of Sulphocyanides and Ferrocyanides from Spent Purifying Mass.—J. V. Esop.—The substance of these papers, which are taken from *Dingler* and from the *Zeit. f. Angewand. Chemie*, has been already noticed.

Determination of Ferric Oxide and Alumina in Phosphates.—E. Glaser (*Zeit. Angewand. Chemie*).—5 grms. of the sample are dissolved in the ordinary manner in 25 c.c. of nitric acid at 1.2 sp. gr. and about 12 c.c. of hydrochloric acid of sp. gr. 1.12, and the whole is made up to 500 c.c. Of the filtered liquid 100 c.c. are put in a $\frac{1}{2}$ litre flask and 25 c.c. of sulphuric acid of sp. gr. 1.84 are added. The flask is let stand for about five minutes, it is shaken several times, about 100 c.c. of alcohol at 95° are added, the flask is cooled and filled up to the mark with alcohol, and shaken briskly. There is produced a contraction. The stopper is withdrawn, more alcohol added, and the flask is again shaken. It is let stand for half an hour and filtered; 100 c.c. of the filtrate (representing 0.4 gm. of the sample) are evaporated in a platinum capsule until all the alcohol is expelled. To the liquid thus freed from alcohol 50 c.c. of water are added in a cylindrical glass and heated to boiling. Ammonia is added until an alkaline reaction appears (not during the boiling). The excess of ammonia is expelled at a boil, the liquid is let cool, filtered, the precipitate washed with hot water, ignited, and the ferric and aluminium phosphates are weighed.

New Use of Oxygenated Water in Analysis.—C. Hiepe (*Chemiker Zeitung*).—Already noticed.

Use of Oxygen in Quantitative Analysis.—M. M. Minor (*Zeit. Angewandte Chemie*).—The author incinerates organic substances in currents of oxygen.

Detection of Small Quantities of Nitrous Acid.—G. Lunge (*Zeit. Angewandte Chemie*).—Already noticed.

Examination of a Common Method for the Determination of Tartar, Tartaric Acid, and Malic Acid.—R. Gans.—From the *Zeit. Angewandte Chemie*.—Not adapted for useful abstraction.

Citric Acid in the Milk of Cows.—F. Soxhlet (*Weiner Land. Zeitung*).—Normal milk contains about 1-1000th of citric acid.

Analysis of Commercial Saccharine.—Ira Remsen and W. M. Burton (*American Chemical Journal*).

Reply to the Above.—Dr. C. Fahlberg (*Chemiker Zeitung*).—A dispute of little general interest.

Detection of Saccharine in Aliments.—B. Fischer (*Neuen Arzneimitteln*).—Tests for saccharine in a variety of admixtures.

Chemical Section of the Industrial Society of Mulhouse.—The business done consisted chiefly in opening "sealed papers," one of which, deposited by M. Jules Persoz, September 12th, 1875 (1), describes a process for dyeing aniline blacks.

Apparatus for Checking the Purification of Gas.—M. Ledig (*Chemiker Zeitung*).—A band of paper saturated with lead acetate is caused to be unrolled in a current of the gas. The paper travels at such a rate that 2 c.m. of length pass hourly into the bell containing the gas.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Medical, 8.30.
 TUESDAY, 15th.—Society of Arts, 8. "Modern Indian Art," by C. Purdon Clarke, C.I.E.
 — Institute of Civil Engineers, 8.
 — Pathological, 8.30.
 — Royal Institution, 3. "The Place of Oxford University in English History," by George C. Brodrick, D.C.L.
 WEDNESDAY, 16th.—Society of Arts, 8. "Old and New Fashions in Typography," by Talbot B. Reed.
 — Meteorological, 7.
 — Geological, 8.
 THURSDAY, 17th.—Royal, 4.30.
 — Royal Society Club, 6.30.
 — Chemical, 8. "Phosphorus Oxide," by Prof. T. E. Thorpe, F.R.S., and Mr. T. E. Fuller.
 — Royal Institution, 3. "The Heat of the Moon and Stars," by Prof. C. V. Boys, A.R.S.M., F.R.S.
 FRIDAY, 18th.—Royal Institution, 9. "Welding by Electricity," by Sir Frederick Bramwell, Bart., D.C.L., F.R.S.
 — Physical, 5.
 SATURDAY, 19th.—Royal Institution, 3. "Colour and its Chemical Action," by Captain W. de W. Abney, R.E., C.B., F.R.S.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1586.

THE VOLUMETRIC ANALYSIS OF COPPER.

By REGINALD A. FESSENDEN,
Chemist, Edison Laboratory, Llewellyn Park, Orange, N.J.

It is well known that the ordinary method of titrating ammoniacal copper solutions by cyanide of potassium contains several sources of error which cannot be entirely removed without considerable waste of time. After a particularly irritating example of this the following experiments were made:—

I. 2 c.c. of copper solution (nitrate with no free acid) taken. Cyanide run in till liquid decolourised. Amount of cyanide solution used, 1.95 c.c.

II. 2 c.c. of same solution taken, made moderately alkaline with ammonia. Amount of cyanide solution used, 2.0 c.c.

III. 2 c.c. of copper solution taken. Large excess of ammonia added. Amount of cyanide solution used, 4.25 c.c.

IV. and V. showed that ammonium nitrate and other ammoniacal salts (as carbonate, &c.), have a similarly disturbing influence.

These experiments showed that it was hopeless to expect accuracy when ammonia was used as a neutraliser. Sodium carbonate suggested itself, and proved exactly what was desired.

VI. 2 c.c. of copper solution taken. 5 c.c. nitric acid added. Made alkaline with sodium carbonate. The clear blue solution was then titrated in the ordinary manner. Amount of cyanide used, 1.90 c.c.

VII. 4 c.c. of copper solution taken. 25 c.c. nitric acid added, sod. carb. added, and titrated. Amount of cyanide used, 3.80 c.c.

VIII. and IX. showed that neither sulphuric nor a mixture of nitric and sulphuric acids have any effect on the result. Analyses were then made of several copper ores, and the results obtained were in the highest degree satisfactory, no matter what variations were made in the amounts of the reagents, provided always that a slight excess of nitric acid is present above that necessary to dissolve the copper sulphide. This condition, however, always obtains in practice.

The end of the reaction is very much more sharp and decided than is the case when ammonia is used, and takes place immediately, so that the tedious waiting at the end of every drop towards the end of the titration is unnecessary.

ON THE EFFECTS OF NITRIC DISSOLUTION.

By H. N. WARREN, Research Analyst.

THE speedy dissolution of a zinc rod, when suspended in contact with such a menstruum as solution of lead acetate, cupric sulphate, or any readily precipitable metal, is always attended more or less by the copious development of a dense spongy metallic mass, which almost instantaneously incrusts the precipitant employed. In the case of a lead salt thus acted upon, which is frequently practised by amateurs with a view of obtaining what is known as the lead tree, the incrustation that is formed, remaining in close proximity to the zinc, is never very striking as regards metallic lustre, and it not unfrequently happens that a considerable course of time has elapsed before the purer quality, which is characterised by its feathery ap-

pearance, begins to develop. If round the zinc rod, however, is wrapped a few coils of asbestos paper before applying the same, on now introducing the zinc into the solution a most interesting modified action accompanies it, the lead being slowly precipitated upon the outer surface of the asbestos. Notwithstanding it being a non-metallic surface, it continues to increase in size, gradually assuming large and perfect octahedrons of metallic lead, the asbestos covering thus acting in much the same manner as the first precipitated or porous quality. If a solution of cupric sulphate be substituted for that of the lead, and the same raised and maintained for some time at the boiling-point, the whole of the copper is precipitated in regular crystals; in short, all the more easily reducible metals may, by the retarding action of the asbestos covering, be obtained in a crystalline form.

Amongst one of the most curious exceptions may be mentioned that of antimony. If to a solution of antimony chloride containing a sufficiency of a tartrate to prevent re-precipitation of basic salts, is introduced the so prepared zinc, part of the antimony is set free, attaching itself in the usual form of crystals to the asbestos covering, whilst a second portion falls in the state of an amorphous black powder, resembling in appearance ordinary lamp-black. This, when raised to an elevated temperature, is oxidised with explosion, being what is known as explosive antimony.

For a further and more complete study of retarded action may be mentioned the withdrawal of the zinc and the replacement of magnesium for the same. By this means zinc was crystallised in a perfectly metallic state, and communicating to the same an arborescent form. Iron, manganese, and even zirconium, were gradually reduced.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

PROFESSOR GRÜNWARD'S MATHEMATICAL SPECTRAL ANALYSIS.

(Concluded from p. 172).

THE view of Dr. Kayser that the comparison with hydrogen and oxygen is used by the author to escape a comparison with the vapour of water is erroneous. As soon as the rhythmic relations of the spectra of hydrogen and oxygen to the spectrum of watery vapour have been established, the rhythmic relations of the groups of rays of one element, *e.g.*, magnesium, to the spectrum of water suffice to indicate its rhythmic relations to hydrogen and oxygen, whether the rays of the latter, ascertained in this manner, can be observed or not. But in the single cases in which the results of sufficiently accurate measurements, *e.g.*, those of the oxygen rays, by Dr. Schuster, agree with the calculated lines, this does not prevent us from seeing in such coincidences a confirmation of the results of the comparison with the vapour of water, or a kind of additional criterion. If in addition along with the predicted wave-lengths, *e.g.*, of oxygen, the author has noted down the less accurate values of Salet and others, he cannot be justifiably held blameworthy on that account. The calculated lines of oxygen and hydrogen are essentially predictions, which are affected by the errors springing from the faults of the material of observation, and thus may be doubted until their accuracy is confirmed by direct or indirect observations.

Of especial importance are those calculated oxygen and hydrogen lines which agree with the corresponding least refrangible lines in the spectrum of the oxy-hydrogen flame, as given by Liveing and Dewar. They can be already tested experimentally, whether they are really oxygen or hydrogen lines, by passing into the oxy-hydrogen flame a gentle current of oxygen or hydrogen, previously ignited, and observing which lines undergo an

intensification. Such lines will probably belong to oxygen or respectively to hydrogen.

The comparison of the calculated hydrogen lines with the solar spectrum of Rowland, or of Müller and Kempf, is of great importance, notwithstanding its unequal accuracy. For even if one of these hydrogen lines was affected with an error of 0.5 Angström unit in either direction, it would indicate a very small region of the solar spectrum, 1 Angström unit in breadth, in which there is situated a hydrogen line not yet recognised as such. Very probably the relatively strongest of the few Fraunhofer lines (2, 3 to 10) situated in this region will be the hydrogen line thus indicated, since enormous masses of ignited hydrogen are contained in the external atmosphere of the sun. If these lines can be experimentally proved to be actual hydrogen lines it will be a new confirmation of the theory.

5. The entire physical and chemical behaviour of a substance is determined by the transverse and longitudinal ether-waves, which, under certain circumstances, combine to form vortex waves, by the fluctuations in pressure and the accompanying currents of the ether. The waves proceeding from two substances, *e.g.*, hydrogen and oxygen, determine, under certain exceptional circumstances, their chemical combination, and thus the waves of a different kind which the compound (*i.e.*, the atomic particles of the components after the establishment of a new dynamic condition among themselves and with the surrounding ether) emit. In consequence the total complex of the waves emitted by a compound (*e.g.*, watery vapour) must be a function of the wave complexes of the two components (*e.g.*, hydrogen and oxygen) in their free condition, and the first complex must be capable of mathematical deduction from the two latter complexes.

The main question which the author has proposed to himself is to ascertain the necessary mathematical connection between the waves which the free constituents emit previous to combination and the waves of a different kind which the compound emits.

The author finds that in the simplest possible cases, in which the primary elements of the constituents undergo an equal or approximately equal condensation, the wave-lengths of the rays produced by their atomic particles undergo a rational modification, and by multiplication into the corresponding factor of condensation they pass into the corresponding wave-lengths within the compounds: the fundamental theorem! Here we have especially to consider only the single rays, the luminous maxima, and the sharp margins of the so-called bands, which the atomic particles of the constituents produce before and after combination. The very manner of putting the question, and the precise definition of the mathematical and dynamical problem, here to be solved is a half discovery.

Here also Dr. Kayser completely misunderstands the real position of matters, and the scope of the thoughts briefly sketched above. He imagines that the author aims at explaining the band-spectra of compounds as such merely by a collocation of certain line spectra, after the latter have been multiplied by rational numbers. He does not consider that our present so-called elements possess, under certain circumstances, visible band spectra, and that the particles which produce such, under other circumstances, in which there appear no visible band-spectrum, do not remain motionless or cease to act upon the ether, though these effects in the latter case have become too feeble to be recognised without especial arrangements, perhaps not yet known.

The author's present position is that of a scientific pioneer and pathfinder, who with imperfect—though constantly improving—arms and instruments, seeks to open up new ways in unknown regions. His position is in this respect very similar to that of Kepler, when he sought to ascertain the laws of the planetary orbits from the observations of his day. His fundamental theorem given above is exactly analogous to the law of Kepler on the ratio of the squares of the time of rotation of the planets

and the cubes of the major axes of their orbits, whilst the plane propositions of the central movements of the stellar world find here their counterparts in linear equations among the reciprocal values of entire groups of the wave-lengths of a substance.

He hopes that the results of his labours may once be better understood, and that in particular he may succeed in making more probable the structure of hydrogen and oxygen as spectrologically determined. The compound nature of oxygen—though unsuspected by many—has already found an indirect but very weighty confirmation from the discovery of Jansen, verified by Liveing and Dewar, that oxygen possesses two groups of rays, which undergo various laws of absorption in condensed oxygen. This fact is of the higher importance as it is a simple consequence of the remarkable structure of oxygen ascertained by the author, and as other bodies of similar composition must possess analogous properties of absorption. —*Chemiker Zeitung*.

EXAMINATION OF CORPSES FOR ALKALOIDS AND OTHER NITROGENOUS BASES.

By Dr. ANTON SEYDA.

(Continued from p. 175).

THE solution of the extract is then divided into three portions. A check test for the possible presence of metallic salts soluble in alcohol must not be omitted.

The first portion is rendered alkaline with potassa-lye, and distilled with the aid of steam. Sometimes it may be needful to distil it in a current of hydrogen. The distillate must be specially examined for nicotine, coniine, and aniline, but it generally yields but little material, consisting of the aminic bases of the fatty series. To this end the distillate is shaken out with ether, the latter is separated and evaporated at a low temperature, preferably in the following manner:—

The flask containing the ethereal extract is placed in water at 70–80° and into it there is passed a moderate current of air. The ether evaporates rapidly at a temperature of about 25°. As soon as its volume is brought to 10 or 20 c.c. the forced evaporation is interrupted, the ethereal solution is poured into a small beaker and allowed to evaporate spontaneously in a warm place.

A constant temperature of 25–40° may be secured as follows:—An air-bath is made by covering a porcelain capsule with a small plate, placing it upon a boiling water-bath, and immersing it more or less deeply according to the temperature required.

The residue after the evaporation of the ether is dried over undiluted sulphuric acid, and ultimately in a partially exhausted receiver. For a closer determination the residue is converted into a neutral hydrochlorate. Above all, the presence or absence of nicotine, coniine, and aniline must be determined. If these bases are absent the attempt is made to obtain the residue in a crystalline form, by preparing, according to well-known methods, double salts with platinum chloride or gold chloride, by dissolving or evaporating in an aqueous or alcoholic liquid at ordinary or at reduced temperatures, or in a vacuum over sulphuric acid. If this succeeds, a determination of the platinum and of the nitrogen, indeed, a complete elementary analysis, followed by a crystallographic determination, will be indispensable.

If no volatile bases are present in the solution, the second portion is shaken out successively with the following liquids:—

1. Ether in a neutral or acid solution.
2. Ether in an alkaline solution.
3. Chloroform.
4. Amylic alcohol in an ammoniacal solution, if in the preliminary examination iodic acid was reduced.

Before passing from one of these shakings-out to the next, the watery solution must be heated and treated with a current of air, to eliminate any residues of the former solvent.

If reactions are obtained which indicate the presence of any alkaloid, the reserved portion of the solution is used for a special examination. The procedure is here modified according to the properties of the alkaloid in question. The solution is mixed with mercuric chloride, and in this general manner the precipitation of the nitrogenous bases is effected. After the lapse of twenty-four hours—not earlier—the precipitate is filtered, washed with sublimate water, and treated further, in known manners, with regard to the demonstration of the special alkaloid.

The residues left after the evaporation of the ethereal, chloroformic, and amylic extracts, are always dried over sulphuric acid. They are sometimes amorphous, sometimes crystalline, and either colourless, yellowish, or brown. They often reduce Frøehde's reagent energetically, with the production of a blue colour, a reaction generally of little importance. The solution of ammonium metavanadate is also reduced, but with a dirty colour. The green colour which generally appears on adding the substance is mostly unimportant.

The ethereal residue obtained from an alkaline solution if heated on the water-bath with officinal (?) phosphoric acid will generally take a more or less distinct reddish violet. This circumstance is important, being regarded as a characteristic of aconitine.

Vitali's reaction with fuming nitric acid and alcoholic potassa, though it occurs beautifully with pure atropine, is in many cases quite worthless. We often obtain residues which show the well-known xanthoproteine reaction more or less plainly, thus quite masking the beautiful violet colour. The pleasant odour so readily obtained with pure atropine cannot be obtained from extractive residues.

Ammonium vanadate, which has of late been warmly recommended as a test for strychnine, is very suitable. The reaction may be effected in a twofold manner. A drop of the vanadic solution may be cautiously mixed with the sulphuric solution of the residue, diluted, if needful, with strong sulphuric acid, and the dry ammonium vanadate is then sprinkled over another portion of the solution as it is done with potassium dichromate.

The advantages of the reaction with ammonium metavanadate, as compared with that obtained with potassium dichromate, are especially distinct with sulphuric solutions of imperfectly pure strychnine. A direct introduction of particles of the residue into the sulphuric solution of ammonium metavanadate, as is done with Frøehde's reagent, is never admissible, since the colour-reactions then come out indistinctly, or not at all, especially in presence of substances which are readily decomposed by strong sulphuric acid. In such cases there often occurs a reduction accompanied with the evolution of sulphurous gas, and thus a coloured reaction may readily be destroyed. In such case the sulphurous acid must be expelled by gently heating the capsule before any further reagent is added.

It must be added that colocynthis gives, both with chromic and vanadic acid, a reaction very similar to that of strychnine, and, as the author believes, not yet publicly known. To produce this reaction a few particles of the extract of colocynth are placed at the edge of the lid of a porcelain crucible and intimately mixed with an equal quantity of pulverised potassium dichromate, but only for a very short time, with the addition of a drop of dilute sulphuric acid (1 vol. acid and 2 vols. water). Strong sulphuric acid is dropped at the opposite margin of the lid, and a narrow streak of the paste is led over to the acid with a thin glass rod. On the contact of both, there appears a fine violet-red colour, gradually increasing in intensity if the mixture of extract is gradually let pass over to the sulphuric acid. This reaction must be initiated very

cautiously, and the strong sulphuric acid must be in excess. If ammonium vanadate is used, the colour produced is at first blue and then reddish.

The amylic residue is often obtained in abundance, colourless, or brown amorphous, or sometimes finely crystalline. Purification by solution in alcohol recommended. The shaking-out in amylic alcohol should always be effected in heat, and the separation of the two strata is promoted by placing the flask in hot water. The amylic alcohol must not be drawn off until completely cold, and evaporation must only be applied to the clear solution after filtration. In this manner, the troublesome property of hot amylic alcohol of taking up not only bases and pigments but water containing various substances will be found less annoying.

The reaction for morphine is best carried out by dissolving the residue in water containing tartaric acid, and adding a solution of iodic acid. As a further reaction may be applied the method for apomorphine. The amylic residues are generally distinguished by their strong reductive action with Frøehde's reagent, which often gives a splendid corn-flower blue.

The watery solution of the extract is tested in the known manner for narceine and curarine.

An examination for the possible presence of metallic salts soluble in alcohol (mercuric chloride, silver nitrate, lead acetate, &c.), though mostly superfluous, should be effected for complete satisfaction.

(To be continued).

AN EXAMINATION OF FUSEL OIL.*

By J. H. LONG and C. E. LINEBARGER.

A FEW analyses of fusel oil are given in the literature, but of these none, as far as we know, have been made of samples of American origin.

The analysis most frequently quoted is that by Rabuteau, while less complete results are given by others. We have attempted to determine, approximately, the composition of a sample of fusel oil obtained at a Chicago distillery, and give the results below.

Most of our American distillers use corn as the chief substance to be converted into mash, with smaller amounts of other grains, and it would therefore naturally be expected that a somewhat different product would be obtained from that produced from a mash of potatoes or beets.

For the purpose of our investigation, several gallons were secured and submitted to distillation, and the other tests given below. This oil has been separated from alcohol fermented during the spring season, by the longer or seventy-two hour period allowed by law. When brought to the laboratory, it was saturated with water and held some in suspension. This was allowed to settle out, leaving a perfectly clear liquid, of which the specific gravity was found to be 0.810 at 20° C. For one series of tests, two litres of this clear oil was dried as thoroughly as possible by shaking it with anhydrous copper sulphate. It was found that all of the water could not be removed in this way. The liquid poured from the sulphate was then treated with dry potassium carbonate, the mixture being kept at a temperature of 40–50° C. for two hours on several successive days. The supernatant liquid was then poured off and distilled nearly to dryness from a retort. Of the distillate thus freed from the water and purified, a litre was taken for a preliminary fractionation. After three complete fractionations the following approximate results were obtained from this sample:—

* From the *Journal of Analytical Chemistry*, vol. iv., Part, 1, January, 1890.

80—90°	17 c.c.
90—95	8
95—105	15
105—115	30
115—120	55
120—125	95
125—130	240
130—133	515
Loss and residue ..	25

The general character of the liquid being shown in this way, larger quantities were operated upon, from which we finally secured several litres boiling above 130°, and correspondingly smaller amounts at the lower temperatures.

Attention was first turned to the portions with higher boiling-points, and at the outset the specific rotation was found for several different samples. For the fractions boiling at the given temperatures, we found in a 400 m.m. tube (Smith and Haensch, large model instrument) at 25° C.—

Fraction.	a_D	d_{25}	$[\alpha]$
120—125°	-3°37'	0·8075	-1°043
125—128°	-3°94'	0·8092	-1°217
128—130°	-3°86'	0·8110	-1°189
130—133°	-3°59'	0·8115	-1°106

From this it is evident that, notwithstanding all our precautions, a considerable portion of the active amyl alcohol passed over below 125° C., with other portions, and this was observed in samples distilled at several different times. An attempt was made to separate the active and inactive alcohols in two of the portions. For this purpose, over a litre of the portion boiling above 130° was treated with sulphuric acid according to the Pasteur method, the mixture of acid and alcohol being allowed to stand for a week, with an occasional gentle heating on the water-bath. The barium amyl sulphate was formed in the usual manner, and crystallised repeatedly in fractions, the less soluble portion being finally reserved. This was converted into the sodium salt by treatment with sodium carbonate. The sodium salt was distilled with sulphuric acid, producing an alcohol which after washing and drying showed a constant boiling-point of 131° and a specific gravity of 0·8116 at 25°. Only 30 c.c. of the alcohol was obtained in the process. When examined in a 100 m.m. polarisation tube, it showed a rotation of $a_D = -0°18'$, from which the specific rotation $[\alpha] = -0°222'$. This is a smaller value than usually given, suggesting, probably, comparative freedom from the active alcohol. An equal degree of success was not obtained in the separation of the latter in a state of purity. For this a litre boiling below 128° was treated in the same manner as before, but only a small amount of alcohol was secured from the more soluble barium amyl sulphate. When washed and dried, the volume amounted to about 20 c.c., and showed a boiling-point 128—129° C. In the 100 m.m. tube this gave a rotation $a_D = -3°50'$, which is a much smaller rotation than reported by Ley, Le Bel, and others.

The preparation of this alcohol from the more soluble barium amyl sulphate is practically a very tedious matter, and it is evident that in our experiments the crystallisations were not carried far enough. But enough was done to show that both alcohols were present in quantity in the fusel oil. From a preliminary examination of the oils obtained from other sources, it appears that the amount of the active alcohol present must in some cases be quite small, as the specific rotations of fractions boiling from 128—133° were often less than $[\alpha] = -0°75'$.

In the distillation of the dried crude oil in quantity, numerous small fractions could be separated between 85—105°, and a considerable portion below 85°.

150 c.c. of this was converted into bromine compounds in the usual manner, by treatment with red phosphorus and bromine, and the product obtained, amounting to

nearly 100 c.c., was washed, dried, and carefully fractionated. We found in this way over 50 c.c. boiling near 40° C. This fraction by subsequent tests was found to consist essentially of ethyl bromide.

35 c.c. was obtained boiling from 61—62° C., which pointed to the presence of isopropyl alcohol in the liquid brominated. Practically nothing was found boiling above these limits.

From the boiling-points of the alcohols taken, it would be possible for butyl alcohol to be present, and this has been reported as a constituent of fusel oils. But we did not succeed in isolating a bromine fraction corresponding to it. The bromide is said to boil at 72° C., but only a very minute quantity was obtained about 62°.

It appears, therefore, that the lower alcohol fractions consist essentially of the ethyl and isopropyl compounds.

It was stated above that no large fraction of alcohol was obtained between 85° and 105°. We took the fraction boiling between 95—105°, and converted it into bromide as before. If normal propyl alcohol existed in the oil, it should be found in the fraction taken, and as it is readily converted into a bromide, we should expect to find some of the latter compound boiling about 71°. In the distillation of the mixed bromides resulting from the reaction, it at first sight appeared that only a trace boiled as low as 71°, but after some little difficulty, we found that the mixture could be resolved into two portions, boiling between 70—73° and 90—94°. That the lower portion actually consisted of normal propyl alcohol was shown by the behaviour of the product on saponification.

The presence of a product boiling between 90—94°, would suggest that in the alcohol fraction brominated, along with the propyl compound, some isobutyl alcohol boiling normally at 108—109° must have been present. In order to gain more accurate information regarding the isobutyl alcohol apparently present, 150 c.c. of the fraction boiling at 105—110° was taken and brominated.

The product obtained after washing and drying amounted to 60 c.c., of which over 50 c.c. boiled at 90—93°. An abundance of the isobutyl alcohol was therefore present in this fraction. It was suspected that the higher fractions, 110—120°, might also contain a not inconsiderable portion. They were subjected to treatment with phosphorus and iodine, the latter being added very gradually, so as to avoid the loss complained of by Chapman and Smith (*Journ. Chem. Soc.*, xxii., 153). 100 c.c. boiling at 110—120°, and 100 c.c. boiling at 120—125°, were treated in this way. The yield was satisfactory. On purifying and fractionating the products, we found 65 c.c. boiling at 121—122°, 20 c.c. boiling at 128—130°, and over 50 c.c. boiling between 140° and 145° C. Below 120° and between 122° and 128° only very small amounts were found. On further fractionating the portion boiling at 140—145°, we found that most of it boiled at 143°, while a little boiled continually higher. It would appear, therefore, judging from the boiling-points alone, that the fractions converted into iodides consisted chiefly of active amyl alcohol and primary isobutyl alcohol, with a smaller amount of normal butyl alcohol.

It may appear singular that so large an amount of iodide with high boiling-point was obtained from the alcohol boiling below 125°, but it must be remembered that this fraction showed also a marked rotary polarisation; in fact, almost as great as with the fraction 125—130°. It is also possible that methylpropylcarbinol was present in the fraction 120—125°, as its boiling-point is only slightly below 120°, and the boiling-point of the iodide 145—146°, but no attempt was made to separate it.

The alcohols of high boiling-point seem to pass over readily with those of lower, but from an experiment carried out by us, it appears plain that the fractions boiling above 125° are but slightly, if at all, mixed with lower alcohols. We converted about 200 c.c. of the fraction 125—130° into iodides, and found that of the purified product only a very inconsiderable portion passed over below 140°.

We have made no attempt to find alcohols or other bodies, present in minute quantity only, in the fusel oil examined, but have sought, rather, to show the characteristic features of the oil. From the foregoing, it appears that it consists chiefly of the active and inactive amyl alcohols, probably three-fourths being made up of these bodies. The next most important substance appears to be isobutyl alcohol, and after that isopropyl and ethyl alcohols, with traces of normal propyl and normal butyl alcohols.

Only a very inconsiderable portion of the original fusel oil possessed a higher boiling-point than 133°. Part of this residue consisted of alcohols, and a part of bodies of an ethereal nature, as shown by simple saponification tests, but the amounts concerned were too small for identification.

THE SPONTANEOUS IGNITION OF COAL CARGOES.*

By Professor VIVIAN B. LEWES,

Associate of the Institution of Naval Architects, F.C.S., F.I.C.

(Continued from p. 178).

On examining the evidence to be obtained as to the conditions under which spontaneous ignition of coal in ships usually takes place, it is found that liability to ignition increases with—

(1) The increase in tonnage of cargoes.

Thus, in cargoes of under 500 tons the cases reported amount to a little under $\frac{1}{4}$ per cent for shipments out of Europe; from 500 to 1000 tons, to over 1 per cent; from 1000 to 1500 tons, to 3.5 per cent; 1500 to 2000 tons, to 4.5 per cent; and over 2000 tons to no less than 9 per cent.

The evidence demonstrating this very remarkable result is to be found in the "Report of the Royal Commission" for 1875, p. 8, and clearly shows the influence of mass upon this action which acts in two ways—

(a) The larger the cargo, the more non-conducting material will there be between the spot at which heating is taking place and the cooling influence of the outer air.

(b) The larger the cargo, the greater will be the breaking-down action of the impact of coal coming down the shoot upon the portions first loaded into the ship, and the larger therefore the fresh surface exposed to the action of the air.

(2) The ports to which shipments are made, 26,631 shipments to European ports in 1873 only resulting in 10 casualties, whilst 4485 shipments to Asia, Africa, and America gave no less than 60.

This startling result is partly due to the length of time the cargo is in the vessel, the absorption and oxidation being a comparatively long action, but a far more active cause is the increase in the action brought about by the increase of temperature in the tropics, which converts a slow action into a rapid one, and if statistics had been taken, most of the ships would have been found to have developed active combustion somewhere about the neighbourhood of the Cape, the active action developed in the tropics having raised the temperature to the igniting-point of the coal by that time.

(3) The kind of coal of which the cargo consists, some coals being specially liable to spontaneous heating and ignition.

This is a point on which great diversity of opinion exists, but I think it will be pretty generally admitted that cases of heating and ignition are more frequent in coals shipped from East Coast ports than in shipments of the South Wales coals. As has been pointed out, however, so much depends on the amount of small coal present

that a well-loaded cargo of any coal would be safer than a cargo of Welsh steam coal in which a quantity of dust had been produced during loading.

The idea that the percentage of pyrites present is any indication of the liability to spontaneous combustion must be entirely discarded, as experiment shows that many coals poor in pyrites frequently ignite, whilst others rich in them are perfectly safe.

A much surer guide is to be found in the quantity of moisture present in an air-dried sample of coal, which is a sure index to the absorptive power; the higher the amount of moisture held by the coal after exposure for some time to dry air, the greater will be its power of absorption for oxygen, and the greater therefore its liability to spontaneous heating and ignition.

This is beautifully shown by a table which follows, in which the percentage of pyrites and moisture present in some coals are contrasted with their liability to self-ignition.

(4) The size of the coal, small coal being much more liable to spontaneous ignition than large.

This, as has been pointed out, being entirely due to the increase in active absorbent surface exposed to the air, a fact which is verified by the experience of large consumers of coal on land; gas-managers recognising the fact that coal which has been stamped down or shaken down during storage being more liable to heat than if it has been more tenderly handled, the extra breakage causing the extra risk.

(5) Shipping coals rich in pyrites whilst wet.

Liability to spontaneous ignition.	Pyrites per cent.	Moisture per cent.
Very slight	1.13	2.54
	1.01 to 3.04	2.75
	1.51	3.90
	1.20	4.50
Medium	1.08	4.55
	1.15	4.75
	1.12	4.85
	0.83	5.30
Great	0.84	5.52
	1.00	9.01

The effect of external wetting on coal is to retard at first the absorption of oxygen and so to check the action, but it also increases the rate of oxidation of the pyrites, and so causes disintegration of the coal, with consequent crumbling and heating due to exposure of fresh dry surfaces.

(6) Ventilation of the cargo.

The so-called ventilation, which has from time to time been introduced into coal ships, is undoubtedly one of the most prolific causes of spontaneous ignition.

For ventilation to do any good, cool air would have to sweep continuously and freely through every part of the cargo, a condition impossible to attain, whilst anything short of that only increases the danger, the ordinary methods of ventilation supplying just about the right amount of air to create the maximum amount of heating. The reason of this is clear. A steam coal absorbs about twice its own volume of oxygen, and takes about ten days to do it under favourable conditions, and it is this oxygen which in the next phase of the action enters into chemical combination and causes the serious heating.

A ton of steam coal occupies 42 to 43 cubic feet, and if properly loaded contains between the lumps as nearly as possible 12 cubic feet of air space, that is to say, of the 42 cubic feet, 12 cubic feet is air and 30 cubic feet is coal.

Thirty cubic feet of coal, with its fresh absorbing surfaces laid bare by the crushing incidental to loading, will, in the first ten days after being taken on board, absorb 60 cubic feet of oxygen, if it can get it. Now, air contains only, roughly, one-fifth of its volume of oxygen, so that 60 cubic feet represent 300 cubic feet of air, or twenty-five times as much as is present; so that it is evident that

* Read at the Thirty-first Session of the Institution of Naval Architects, March 28, 1890; the Earl of Ravensworth in the Chair.

if air could be excluded there would be only one twenty-fifth the quantity of oxygen present which is needed for complete action, and any heating would, in consequence, be very slight; whilst to produce the greatest heating it would be necessary to change the entire air in the cargo twenty-five times in the first ten days, and this is just about what the ordinary method of taking a box shaft along the keelson with Venetian lattice upshafts from it would give.

The most forcible illustration of the evil of such ventilation is to be found in the case of the four colliers, *Euxine*, *Oliver Cromwell*, *Calcutta*, and *Corah*, which were loaded at Newcaste under the same tips, at the same time, with the same coal, from the same seam. The first three were bound for Aden, and were all ventilated. The *Corah* was bound for Bombay, and was not ventilated. The three thoroughly ventilated ships were totally lost from spontaneous ignition of their cargo, whilst the *Corah* reached Bombay in perfect safety.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

March 20, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

Messrs. Bertram Blount, S. Home Collins, F. H. Perry Coste, T. S. Dymond, and W. Charles Sayers were admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Dixon, 3, Belle Vue Park, Sunderland; Thomas Flower Ellis, Widmore, Bromley, Kent; Frederick John Hambly, 13, Osborne Place, Dundee, N.B.; Charles Terry Holloway, 188, Lewisham High Road, S.E.; John Stewart MacArthur, 46, Melville Street, Pollokshields; Harold Pigton, 80, Regent's Park Road, N.W.; Alexander Smith, 4, West Castle Road, Edinburgh.

The following lecture was delivered:—

"The Evidence Afforded by Petrographical Research of the Occurrence of Chemical Change under Great Pressure."
By Professor J. W. Judd, F.R.S., F.G.S., &c.

The materials constituting the deeper parts of the earth's crust must sustain great static pressure, due to the weight of superincumbent rock masses; some of these materials, too, have from time to time been subjected to enormous dynamical pressures resulting from the stresses which arise during mountain-making and other earth-movements. Hence it is found that the rocks and minerals which have at any time formed the deeper parts of the earth's crust show many striking evidences of the action of these pressures: among these may be mentioned the cavities filled with various supersaturated solutions, carbon dioxide, and other materials; there are also remarkable indications of strain, distortion, and fracture presented by the minerals when their optical properties are studied.

The question was discussed how far the phenomena observed by the geologist in his study of rocks under the microscope can be explained by the laws that have been experimentally determined by the physicist and chemist; and it was pointed out that the conclusions to which both the experiments of physicists and chemists and the observations of mineralogists and geologists point are as follows:—

1. In all those cases in which crystallisation is accompanied by contraction, the tendency of pressure is to promote the change from an amorphous to a crystalline condition.

2. Crystallised minerals developed in a magma under

pressure may lose their stability, and be dissolved by the same magma when the pressure is removed.

3. In all those cases in which solvent action is accompanied by contraction, dissolution is promoted by pressure.

4. Under great static pressures the whole substance of solid bodies may be permeated by fluids (liquids and gases alike), and chemical action between these and the solids is thus greatly facilitated.

5. By the intimate admixture, under great static pressures, of solids with fluids, the properties of the former are remarkably modified.

6. Mechanical stresses, which tend to overcome the attraction between the particles of a solid, promote chemical action at those parts of the mass which are in a condition of intense strain.

7. Pressure may supply the conditions required for the renewal of the growth of crystals when their development has been arrested for an indefinite period, and even after they have suffered mechanical injuries.

8. When dissolution under pressure is going on in a crystalline substance, the action is controlled and modified by its molecular structure; this structure having been produced in the process of crystallisation, or having been acquired by the crystal subsequently, owing to the action of mechanical and other forces upon it.

9. Under great pressures, paramorphic changes take place in crystalline substances without change in their chemical composition.

10. Both the dissolution of existing compounds and the formation of new crystallised minerals may result from pressure; and these two operations frequently going on together, pseudomorphs are produced, the action sometimes affecting great rock masses.

11. When, as the result of dynamical pressures, the crystalline constituents of rocks are brought into close contact, chemical affinities come into play between them, and new mineral species result from the interactions. This operation is facilitated when, as the result of internal strains, differential movements are set up in a rock mass, and rubbing or sliding contacts between the particles are brought about.

12. When internal strains and differential movements affect a mass in which the process of crystallisation is going on, the forms and positions of the crystals may be modified. The structures known to geologists as "granulitic" and "foliated," which characterise the crystalline schists, have been produced in this way, as was shown by Scrope, Dana, Darwin, Sharpe, and Naumann, and confirmed by many subsequent investigators.

In arriving at these conclusions recourse has been had only to proved causes of change, and hypothetical causes have been avoided. Some of them may seem insignificant, but, affecting, as they have done, vast masses of material during enormous periods of time, the results accomplished by such apparently insignificant causes have been very great.

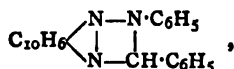
Although dynamical pressures may be converted into heat, as shown by Mallet, or into chemical action, as argued by Sorby, no very distinct evidence of great effects having been produced by these methods has been discovered.

The following papers were read:—

21. *"The Formation of Triazine Derivatives."* By R. MELDOLA, F.R.S.

In consequence of a recent paper by Goldschmidt and Rosell (*B.*, 1890, 487), which to some extent anticipates an investigation upon which the author and C. Tyrer have been at work for some time, the method adopted for the synthesis of triazine derivatives is briefly described in this communication. The method consists in acting on a benzyldine derivative of an amine with a diazo-salt so as in the first place to form an orthazo-compound; on heating a solution of the azo-compound, preferably in

glacial acetic acid, the benzylidene and azo-groups then undergo condensation, forming a triazine ring. In this way diphenyl- $\alpha\beta$ -naphthotriazine, having the formula



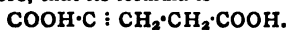
has been prepared from benzylidene- β -naphthylamine and diazobenzene chloride. It is a feeble base forming dense flat white needles melting at $193-194^\circ$, dissolving with difficulty in benzene and but very sparingly soluble in alcohol. Other triazine derivatives prepared by this method are in course of investigation.

22. "Contributions to the Knowledge of Mucic Acid. Part I., Hydromucic Acid." By S. RUHEMANN, Ph.D.

Chloromuconic acid, prepared from mucic acid in accordance with Bode's directions (*Annalen*, cxxxii., 195), is very stable, as indeed Limpricht has already stated; its chlorine is not displaced by the action of boiling alcoholic potash or ammonia; aniline acts very readily on its alcoholic solution, but the product is simply the aniline salt. Its ethylic salt is converted by ammonia into chloromuconamide.

The authors find that chloromuconic acid is most conveniently converted into hydromucic acid by treatment with tin and chlorhydric acid. Of the two possible formulæ of this acid, $\text{COOH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ and $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$, there can be no doubt that the former is to be regarded as correct, as v. Baeyer has shown that hydromucic acid is obtained on reducing the dicarboxylic acid, $\text{COOH}\cdot\text{C}:\text{C}:\text{C}\cdot\text{COOH}$.

It appears that, contrary to Limpricht's statement, the same dibromadipic acid is obtained by the action of bromine on hydromucic acid when acetic acid is taken as solvent as when water is used. The acid melts at $185-207^\circ$, according to the rate of heating. Ethylic dibromadipate, prepared either directly from the acid or by brominating ethylic hydromuconate, crystallises in long needles melting at 64° ; by the action of ammonia, this salt is converted into the amide of an acid isomeric with muconic acid. This isomucic acid, $\text{C}_6\text{H}_6\text{O}_4$, can be easily obtained by heating ethylic dibromadipate with alcoholic potash; it crystallises in white fine needles, very sparingly soluble in water and alcohol. The barium, lead, potassium, silver, and ethylic salts of this acid are described. On oxidation with permanganate, isomucic acid yields oxalic and succinic acids, and there can be no doubt, therefore, that its formula is—



23. "The Molecular Weights of Metals when in Solution." By C. T. HEYCOCK, M.A., and F. H. NEVILLE, M.A.

In a previous communication (*Proc. Chem. Soc.*, 1889, p. 41) the authors have given a preliminary account of their observations on the effect of metals on the solidifying point of tin, and they subsequently described similar experiments using sodium as the solvent (*Chem. Soc. Trans.*, 1889, 666). They now give the details of the investigation of solutions in tin.

Tables of results are given showing the effect of various proportions of the following metals:—Silver, gold, copper, nickel, sodium, palladium, magnesium, zinc, lead, cadmium, mercury, bismuth, calcium, indium, aluminium, and antimony. Of all these metals, antimony alone behaves abnormally, producing a rise instead of a depression in the solidifying point.

An example will illustrate the method of calculating the "atomic depression." In an experiment with silver, 4.3085 grms. were dissolved in 400 grms. of tin, i.e., $\frac{4.3085}{108}$ of an atomic proportion; and therefore there was present per 100 proportions of tin—

$$\frac{4.3085 \times 118 \times 100}{108 \times 400} + 1.177$$

atomic proportions of silver. The observed solidifying point of tin was 231.68° , and of the solution 228.29° , a depression of $231.68 - 228.29 = 3.39^\circ$; hence the atomic depression was—

$$\frac{3.39}{0.177} = 2.875.$$

In the majority of cases, the atomic depression is a number not far removed from 3. If Raoult's generalisation be true, that the depression produced by a molecular proportion of any substance in the solidifying point of the same solvent is the same whatever the substance, it would therefore seem probable that the molecules of most metals are of the same type, M_n , where n is the number of atoms in the molecule; and if it be supposed that the molecules of, say, zinc, when dissolved in tin, are monatomic, as in the gaseous state, it would follow that n is unity in the case of many other metals. The theoretical depression calculated from Van't Hoff's formula is 3, and a similar value may be deduced from a formula suggested by Professor J. J. Thomson. In the case of aluminium, the atomic depression is so nearly half the average value that it seems probable that the molecule is diatomic. Indium resembles aluminium in producing an abnormally low depression; and it is noteworthy that the value for mercury is distinctly low: in fact, the data recorded show that there are many interesting points of difference to be noted between the various metals.

Annual General Meeting, March 27th, 1890.

The President delivered an address, of which the following is an abstract:—

There are at present 1733 Fellows of the Society of whom 34 are honorary foreign members; at the same period last year there were 1650, including 36 honorary foreign members.

145 Fellows have been elected during the year.

16 Fellows have died during the year:—Richard Anderson, M. T. Buchanan, M. Chevreul (foreign member), John Dale, Dr. Warren de la Rue, Ernest H. Francis, Prof. A. Geuther (foreign member), James Hindle, J. P. Joule, Benjamin Nickels, Henry Pollock, Owen Prosser, Dr. R. Romanes, Dr. Edmund Ronalds, Joseph Stapleton, Dr. David Waldie.

12 Fellows have withdrawn:—S. F. Burford, E. B. Clarke, N. M. Falkner, Alex. Galt, John Innes, Alfred Neild, W. F. Pankhurst, Forbes Rickard, Newton Samuelson, Rev. S. D. Titmas, Wm. Weston, G. H. With, Charles Williams.

34 Fellows have been removed from the Society's list on account of arrears:—G. W. Arnott, A. B. Avarne, W. Alabaster, W. A. Bradbury, F. W. Drinkwater, Joseph Fletcher, F. W. Fleming, T. H. Judson, Chas. A. R. Jowett, T. N. Kirkham, John W. King, R. W. E. MacIvor, E. C. L. Muspratt, K. D. Naegamvala, W. O. Nicholson, Rev. P. R. Ogle, J. B. Orr, C. H. Piesse, A. N. Pearson, Victor E. Perez, A. E. Robinson, Alfred Southall, J. Schwartz, Frederick Sear, F. W. Simpson, J. H. Thompson, John A. Tate, Caleb Terry, John D. Veira, Peter H. Walsh, R. N. Wolfenden, H. P. White, Edward Willmore, and Chas. F. Young.

100 papers have been communicated to the Society during the session; a considerable number of these have, at their authors' request, been published in the *Proceedings*, now in the sixth year of its existence, and which has become a most valuable adjunct to the Journal, serving to give as wide and as important a publicity to a paper as the *Transactions*, and at the same time affording a rapidity of publication not exceeded by any other scientific journal.

In the year 1889, 71 papers, occupying 773 pages, have been published in the *Transactions*; 75 papers, occupying 895 pages, having been published in the year 1888. The number of abstracts published during 1889 is 2131, which

occupy 1252 pages; the number is considerably smaller than in the previous year, when it was exceptionally large, viz., 2470, occupying 1351 pages.

After speaking with approval of the work done by the Publication Committee and the Editors, the President said that it was intended to give more attention in future to the abstracts of analytical papers, and to illustrate these when necessary; and referring to the fact that next year the Society will have been in existence fifty years, he said that it had been suggested that the issue of a complete subject catalogue of the Society's original publications would be a fitting memorial of the occasion; such a work was practicable, and the Society had the means of carrying it out.

Not only had the Library Committee procured a considerable number of new books during the year, but by the generosity of several Fellows and others, and by purchase, a very important addition had been made to the Library of old books. The importance to the Society of a complete collection of historical works could not be overrated: the Committee lose no opportunity of securing such works, but they trust that Fellows will, whenever possible, assist their efforts in this direction, and he would remind them how much the value and interest of an old book is increased when it becomes an integral part of a series of historical works such as the Society already possesses. The present state of the Library shelves is shown in the following table:—

	March 31st, 1889.	Additions in 1889-90.	Present state.
Volumes of systematic works	2,922	160	3,082
Volumes of journals . .	5,474	193	5,667
Volumes of duplicate journals for circulation	1,084	51	1,135
Pamphlets	1,426	24	1,450
	10,906	428	11,334

The expenditure under this head during the year had been £270 18s. 11d.

During the year the Royal Society had awarded both the Davy and a Royal medal to Fellows of the Society, and he felt sure, said the President, that all rejoice that the important investigations of Dr. Perkin and of their Treasurer, Prof. Thorpe, had met with such well deserved recognition of their value.

Referring to the alteration which had been made in the time of the anniversary meeting, and to the dinner which was to take place in the evening, the President said that it had been thought that it would be of advantage to the Society in general to follow the example of other societies and to have an anniversary dinner; and it was hoped that the change would have the effect of bringing a large number of Fellows together, and that those not resident in London would feel it to be a duty as well as a pleasure to attend at least the annual evening meeting of the Society.

The recent important lecture for which the Society was indebted to Professor Judd was referred to. Attention was then drawn to the special meeting for the exhibition of apparatus to be held on May 8th next; in every active laboratory there is to be found apparatus devised to meet some special requirement which has not been made known, which can be appropriately shown at such a meeting.

The President then proceeded to discuss the teaching of chemistry to medical students. It was too seldom recognised that the fundamental action of medicines—the origin of their power—is a chemical change, and hidden and complicated as are the changes produced by medicines, they must ever retain their chemical character; if an understanding and appreciation of their effects is to be sought for, the first step must be to learn the laws which govern chemical action, and the chemical nature of the substances employed. But in addition to furnishing

so many of the elementary facts on which the rational practice of medicine rests, chemists may claim that a better schooling cannot be devised for the student of medicine than that afforded by the study of these facts in their simplest form. Reference was made to the Reports of the British Association Committee on the Teaching of Chemistry in Schools, and to the influence exercised by the Science and Art Department on the teaching of chemistry throughout the country, in proof that, however imperfect the system of teaching has been, attention is now drawn to the importance of effecting an improvement, and that it is to be expected that the number of students will rapidly increase, and that the quality of the teaching will advance.

While protesting most emphatically against the exclusion of chemistry from the medical curriculum, the President said that chemists had, he thought, unduly urged an extensive knowledge of their science as necessary to the medical man; he would willingly relinquish the idea of making him a chemist, but he most pertinaciously adhered to the statement that he must be well trained in elementary chemistry. If students were encouraged to regard elementary knowledge as of no use and the methods by which knowledge is gained from experiment as of no avail to them, we should be educating them to become empiricists instead of fitting them to become observant and reasoning human beings. He thought that chemistry should be placed in the same category as the recognised subjects of general education, and made obligatory in the preliminary examination; all students on commencing their career at the medical school would then have some knowledge of the subject: the teacher there would commence his instruction at a higher level than at present, and would be able to enforce his teaching by preference by means of illustrations having a technical bias. The Examining Board of the two Colleges insists in the case of anatomy, medicine, and physiology that the student shall have studied at a recognised medical school, thus recognising most wisely the importance of study under efficient instructors and at places properly equipped; he desired to protest most strenuously against the exclusion of chemistry from this healthy regulation. At present the candidate, on presenting himself for examination in chemistry, has but to produce a certificate stating that he has received chemical instruction; if only qualified persons gave certificates these would be of value; as it is, he failed to see the use of the certificates. A strong feeling is growing up that a most valuable, if not indispensable, adjunct to examinations is the knowledge where the student has studied, and the guarantee that he not only has had proper and sufficient opportunities, but also that he has made use of them. If all restrictions be waived in the case of chemistry, and everything be allowed to depend on an examination, the examination must be made far more searching than at present, and in place of hours must last for days.

It would be of great advantage to the medical student to direct his attention to chemistry at two distinct periods; and, in addition to the elementary class, there should be in every medical school a higher class for students who have time and inclination for the more thorough study of the subject. The teacher of physiology and the teacher of chemistry should work together far more than is now the case; at present the student regards the chemistry of the chemical teacher as something distinct from and not nearly so necessary as the chemistry of the physiologist.

The Fellows of the Society could best realise the advantages to be derived from the careful and accurate study of chemistry, and it must devolve on them, while not blind to the importance of other studies, to advocate that chemistry should be assigned its proper place, and should be efficiently taught, not only to the medical student, but as a branch of a liberal and general education to all other students.

Sir F. A. ABEL proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; Professor EMERSON REYNOLDS seconded the motion; Mr. CASSAL then spoke on behalf of the motion, in order to give expression to his views as to the status of Fellows of the Society. The motion was carried by acclamation. The President having acknowledged the vote,

Professor THORPE, the Treasurer, gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3637; by sale of the Journal, £377 3s.; and by dividends on invested capital, £340 10s. 9d. The expenses on account of the Journal had been £2310 18s. 3d.; on account of the Proceedings, £177 4s. 7d.; on account of the Library, £420 8s. 11d.; the total expenditure being £3578 18s. 8d. £530 had been invested in Metropolitan Board of Works 3½ per cent stock, and the balance in hand was £2056 2s. 7d., as against £1833 13s. 6d. for the corresponding period last year.

Dr. H. MÜLLER proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; the motion was seconded by Professor DUNSTAN.

Professor THORPE, after replying, proposed a vote of thanks to the Auditors, Messrs. R. H. Davies, Bernard Dyer, and R. J. Friawell; this was seconded by Mr. F. J. M. PAGE and acknowledged by Mr. DAVIES.

A vote of thanks to the Officers and Council, having been proposed by Mr. CARTEIGHE and seconded by Professor RAMSAY, was acknowledged by Professor THOMSON.

Mr. WARINGTON moved that thanks be tendered to the Editors, Abstractors, and Librarian; Mr. PICKERING seconded the motion; Mr. GROVES replied.

Mr. T. Fairley and Mr. Wm. Thorp having been appointed scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President—W. J. Russell, Ph.D., F.R.S.

Vice-Presidents who have filled the Office of President.

—Sir F. A. Abel, C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—Dr. A. Crum Brown, F.R.S.; G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.; J. W. Mallet, M.D., F.R.S.; J. Emerson Reynolds, M.D., F.R.S.; Robert Warington, F.R.S.

Secretaries—H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary—F. R. Japp, LL.D., F.R.S.

Treasurer—T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council—Henry Bassett; Norman Collie, Ph.D.; C. F. Cross; Wyndham Dunstan; John Ferguson, M.A.; E. Kinch; Raphael Meldola, F.R.S.; M. P. Muir; F. J. M. Page; S. U. Pickering, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.

Society of Arts.—The papers for the Wednesday evening meetings after Easter to the end of the session have been fixed as follows:—On April 16, "Old and New Fashions in Typography," by Talbot B. Reed; April 23, "Coal in the South-East of England," by William Whitaker, F.R.S.; April 30, "Photographic Lenses," by T. R. Dallmeyer; May 7, "The Aim and Scope of Higher Technical Teaching," by Dr. Percy F. Frankland; May 14, "Professor Elihu Thomson's Electro-Magnetic Induction Experiments," by Dr. J. A. Fleming; May 21, "The Mannesmann Process for making Seamless Tubes," by J. G. Gordon.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 12, March 24, 1890.

Condensations of Carbon Monoxide and the Penetrability of Glass by Water.—M. Berthelot.—The author calls attention to the aptitude of carbon monoxide to form condensed and polymerised compounds stable only at temperatures below redness. The condensed product is brownish with a white portion on its edges. It attracts moisture from the air with extreme rapidity. The penetrability of glass by water under electric influence, if it can be conceived of as possible with certain exceptional glasses, does not appear to constitute a general phenomenon.

Remarks on M. Berthelot's Observations on the Reactions between Vegetable Mould and Atmospheric Ammonia.—Th. Schloësing.—All the discussions in the world are not worth a fact well observed. The fact of the absorption of aerial ammonia by vegetable soil is now well observed and is a general fact.

New Preparation of the Betaines.—E. Du villier.—The author has arrived at very good results by causing a hydriodic ether to act upon a zinc salt of the amidic acids in presence of zinc oxide, a process analogous to that which enabled M. Schützenberger to obtain the leucines synthetically.

Determination of Acetone by Iodoform.—G. Arachequesne.—The author recommends that Krämer's method, as it stands, should be employed only for pure methylic ether. For methylated spirit containing from 1·5 to 30 per cent of acetone he uses the same method, but takes a relatively smaller volume. For spirit of 20 to 30 per cent he takes 5 c.c. and dilutes with water to 500 c.c. Of this mixture he takes 5 c.c. and multiplies the result by 20.

On Callose, a New Fundamental Vegetable Substance Existing in Membrane.—Louis Mangin.—The author has not yet obtained this substance in a state of purity, so as to determine its composition. It is colourless, amorphous, insoluble in water, in alcohol, and in Schweitzer's reagent; very soluble in caustic alkali at 1 per cent, soluble in the cold in sulphuric acid, calcium chloride, and strong stannic chloride; insoluble in cold alkaline carbonates and ammonia, which gelatinise it. It is coloured by aniline blue and rosolic acid and certain azo-colours.

Determination of Fatty Matter in Milk.—M. Lezé.—The author takes a glass flask with a long neck graduated in c.c. and tenths of a c.c. He pours into it a mixture, already prepared and agitated, of 100 parts of the milk and 200 to 250 parts of pure strong hydrochloric acid, and heats until the liquid turns brown. He then adds dilute ammonia until the liquid becomes clear, and lastly hot water until the level reaches the height of the graduation. He then reads off the number of divisions occupied by the fatty matter. This butter has a sp. gr. close upon 0·90, and by multiplying the volume observed by this factor we have the weight.

No. 13, March 31, 1890.

Observations on the Foregoing Communication and on the Desiccation of Gases.—M. Berthelot.—The author still entertains doubts on the origin of the moisture observed by M. Schützenberger. He does not think the penetrability of ordinary glass by water proved, and supposes that the interior of the glass tubes and the mercury may have been slightly damp.

Condensation of Carbon Monoxide.—P. Schützenberger.—In reply to M. Berthelot the author maintains that the two chief conclusions in his paper of March 17 are not contradicted by the experiment described by the latter.

Conductivities of Phenols and Oxybenzoic Acids.—Daniel Berthelot.—The three isomeric oxybenzoic acids have quite distinct conductivities, decreasing in the order ortho-, meta-, para-, the conductivity of the latter approaching that of benzoic acid.

Refraction-Indices of Saline Solutions.—B. Walter.—The author objects to the conclusion of M. Doumer that the molecular refractive powers of the salts are functions of the number of valencies of the metallic element which enters into the composition of the salts. He holds, on the contrary, that the molecular refringent power of copper and iron sulphates is triple that of potassium and sodium chlorides and $\frac{1}{2}$ that of potassium and sodium sulphates.

Action of Sodium Thiosulphite upon the Salts of Silver.—J. Fogh.—The author maintains that on thermo-chemical principles the solution of silver iodide in thiosulphite is not possible without the assistance of some extraneous energy. This result is confirmed by experiment. A solution of the double silver and sodium thiosulphite is precipitated by potassium iodide, whilst it is not affected by the addition of a solution of a chloride or a bromide.

Pre-Columbian Metallurgy in Venezuela.—V. Marcato.—An analysis of three metal trinkets recently found near Caracas in some earthen sarcophagi containing bones. One of these has probably been formed by the hammer from native gold, very rich in silver and containing copper. The other two are alloys of argentiferous gold with a product of the reduction of an ore of copper and iron. Near the site there occurs a vein of copper carbonate intimately mixed with iron oxide, but containing neither gold nor silver.

Influence of the Chemical Constitution of the Derivatives of Carbon upon the Direction and the Variations of their Rotatory Power.—P. A. Guye.—The author draws the following conclusions:—Whenever, in consequence of the substitution of an element or radicle by another, the centre of gravity of the molecule remains on the same sides of the planes of symmetry of the carbon, the rotatory power of the substituted derivative thus obtained must retain the same sign. If, in consequence of a substitution, the centre of gravity of the molecule is removed from the planes of symmetry, the rotatory power of the substitution-product must be greater than that of the original substance. On the contrary, it will be smaller if the centre of gravity approaches the planes of symmetry. If, in consequence of substitution, the centre of gravity is displaced from one side to the other of one of the planes of symmetry, the rotatory power of the new product changes its sign.

Preparation and Properties of Fluoroform.—M. Meslans.—The gas is colourless; it burns with difficulty, giving off much hydrofluoric acid and colouring the flame blue. Its odour resembles that of chloroform. It is sparingly soluble in water, chloroform, and benzene; alcohol dissolves about 5 vols. The sp. gr. is between 2.48 and 2.53; theoretically it would be 2.44. It liquefies at 20° under a pressure of 40 atmospheres, and solidifies at higher pressures. If heated to 160° in a sealed tube with alcoholic potassa it is split up into potassium fluoride and formate. The composition of the gas is CHF_3 .

Sulpho-Conjugated Phenols derived from Ordinary Camphor.—P. Cazeneuve.—Concentrated sulphuric acid in the cold gives, with monochlorocamphor, a mixture of sulpho-conjugated compounds having a phenolic function. This formation proves that the terebenic series contains the benzene nucleus, and is merely a branch of the aromatic series.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6.

Method for Determining Quinine in Quinine Tannate.—Dr. Sig. Neumann.—The author weighs out exactly 2 grms. of pulverised quinine tannate, and introduces it into a glass cylinder holding about 300 c.c., and having a well-fitted stopper, previously charged with 20–25 c.c. potassa-lye (sp. gr. 1.240), and shakes the whole well up. Care must be taken that the tannate does not adhere to the sides of the glass, as it is there not easily removed by the potassa-lye. The whole is then made up to 60–80 c.c. and 100 c.c. ether, accurately measured, are added, the stopper is rapidly inserted, and the whole is shaken well together. After a few minutes, there appear two separate layers of liquid, the colourless ether above and below the potassa-lye coloured brown by the tannin. No solid particles should be floating about in either. If the potassa is so dark as to be opaque, it is diluted or the cylinder is laid horizontally and observed from above. After the two strata have completely separated, the cylinder is unstopped, 50 c.c. of the ether are quickly measured off with the pipette, and poured into a weighed beaker. The ether is allowed to evaporate slowly at a temperature of 50–60°, and the residue (quinine anhydride) is dried at 100°. When cold, it is weighed, and if two grms. of the substance were originally taken, we have at once the percentage. The residue can be examined for other alkaloids. It should be perfectly soluble in dilute hydrochloric or sulphuric acid, otherwise either the ether was impure or fats or resins were present in the sample.

Detection and Determination of Chlorine in Alkaline Sulphocyanides.—C. Mann.—If an alkaline sulphocyanide is mixed with a solution of copper sulphate and treated with sulphuretted hydrogen, there falls at first only white copper sulphocyanide, which on prolonged action passes into copper sulphocyanide. If more copper is present than suffices for the formation of copper sulphocyanide, and if the current is interrupted at the moment when the liquid becomes brown, and if a corresponding quantity of fresh solution of copper is added to take up the free sulphuretted hydrogen and precipitate any hydro-sulphocyanic acid which may have become free, the filtrate no longer gives the sulphocyanide reaction. If, therefore, there was in the sulphocyanides used only a very trifling quantity of chlorine or bromine, it can be easily detected by the addition of a little nitric acid and a few drops of dilute silver nitrate. The mixture of copper sulphocyanide and sulphide can be easily filtered, and the filtrate never runs through turbid on washing. In practice, 5 grms. of the sample at most are taken, and require 20 grms. pure copper sulphate, which may be kept ready in solution of the strength 20 : 100. Both salts, each dissolved in 100 c.c. of cold water, are poured together, sulphuretted hydrogen is passed in, and 8 grms. copper sulphate, 40 c.c. water are added, well stirred, and the precipitate is filtered off. The chlorine in the filtrate is determined in the ordinary way as silver chloride.

New Extraction Apparatus.—Dr. O. Knöfler.—This paper requires the accompanying cut.

New Porcelain Capsules for Quantitative Work.—Dr. O. Knöfler.—The author's improvement consists in introducing a dark green or black lining-colour under the glaze, so that light-coloured—especially amorphous—precipitates may be seen more readily.

Distinction between Propylic and Butylic Alcohol.—Normal propylic alcohol has the sp. gr. 0.813, boils at 97°, is readily soluble in water, and if rubbed on the hands has a pleasant fruity smell. If its solution in 30 per cent spirit is shaken with chloroform it is not taken up. Butylic alcohol (fermentation) has the sp. gr. 0.805; it boils at 108–109°, dissolves with difficulty in water, floating on the surface like oil; it has an unpleasant oily fusel smell if rubbed in the hands, and is taken up

Chloroform with increase of volume. If crude spirit diluted to 30 per cent is shaken up with chloroform, amyl alcohol, acetol, aldehyd, and (fermentation) butylic alcohol are extracted, whilst ethylic alcohol, acetic acid, and tertiary butylic alcohol remain in the supernatant liquid.

Apparatus for Fractionated Distillation at Reduced Pressure.—E. Valenta.—This paper requires the five accompanying figures.

Laboratory Apparatus.—Dr. A. Burgemeister.—These appliances consist of a gas-generating apparatus, a filter-bell, and a sulphuretted hydrogen apparatus, all figured.

Apparatus for Emptying Gas-Generators.—A. C. Hertzog.—This paper requires the two accompanying cuts.

New Potash Apparatus.—S. Schiff.—This paper cannot be reproduced without two woodcuts.

Determination of Copper by Converting the Sulphide into Oxide.—C. Holthof.—On working with precipitates of 0.18–0.22 grm., the author observes that precipitated copper sulphide, filtered in a suction-pump, introduced, while still moist, into the crucible, and treated exactly according to Bunsen's directions, smoulders at a moderate temperature of the crucible, and passes readily into copper oxide, so that, on subsequent ignition over a good burner for seven to ten minutes, there is no further loss of weight on re-ignition, nor can any trace of sulphuric acid be found in a solution of the residue. Dried precipitates of copper sulphide, even after ignition for hours, still retain traces of sulphuric acid.

Hygrometric Methods.—W. N. Shaw.—From the *Philosophical Transactions*.

Determination of the Specific Gravity of Pulverized Substances.—W. F. Smeeth.—From the *Scientific Proceedings of the Dublin Society*.

Determination of Specific Gravity of Fluids.—A. B. Taylor.—From *American Journal of Pharmacy*, per CHEMICAL NEWS.

Absorption of Gases in Liquid Mixtures.—O. Müller and O. Lubarsch (*Annalen der Physik und Chemie*).

Absorption and Condensation of Carbonic Acid on Clean Surfaces of Glass.—H. Krause (*Acad. des Sciences, Petersburg*).—In the absence of water there occurs no condensation or absorption of the gas. If water is present, condensation takes place more abundantly if the surface of the glass is rich in alkali.

Tension of Watery Vapour over an Aqueous Solution of Caustic Potassa.—G. Errera (*Gazzetta Chimica*).—Merely mentioned.

Separation of Precipitates difficult to Filter from the Liquid.—E. Bauer (*Chemiker Zeitung*).—The author moves the liquid by diffusion. He takes a funnel without neck, ground off below rather broad so that the point of a filter may project out downwards. If the funnel thus prepared is set on a vessel of water into which the point of the filter dips, and the precipitate and mother-liquor are introduced, the solution will diffuse into the water, and can be entirely removed by the use of successive quantities of water.

Apparatus for the Rapid and Correct Measurement of Liquids.—G. P. Vanier (*Journal of Analytical Chemistry*) and B. Gerdes (*Chemiker Zeitung*).—For the description of these appliances we must refer to the originals.

Filtering Arrangements.—An account of the apparatus of G. Neumann (*Journal für Prakt. Chemie*), G. C. Bone (*Journal of Analyt. Chemistry*), and L. L. de Lönnick (*Zeitschrift Angewandte Chemie*). The last proposes that the filtration of precipitates which require to be dried and weighed on the papers should be effected in small light funnels capable of being weighed.

Colorimeters.—A brief mention of Lovibond's tintometer, from the *Journ. Soc. Chem. Industry*, and also of M. Müller's colorimeter for Nesslerising water (*Dingler's Journal*), and of Ad. Jolle's colorimeter. The two latter depend on well-known principles.

A Normal Barometer.—P. N. Raikow (*Chemiker Zeitung*).—A syphon barometer with a mercury level which can be displaced, as in Fortin's barometer.

A New Barometer with an Air Thermometer.—F. C. G. Müller (*Annalen der Physik*).—For the description of this instrument we must refer to the original.

Vaporimeter for Determining the Tension of Vapours at the Temperature of Boiling Water.—G. Th. Gerlach (*Chemische Industrie*).—This instrument differs chiefly from one formerly described by the same author by the method of heating which takes place in two concentric tubes filled with steam.

MISCELLANEOUS.

Determination of "Total Residue" in Water Analysis.—Wm. P. Mason.—Water residues, particularly those from mineral waters, are often so hygroscopic as to be exceedingly difficult to weigh, if the evaporation be performed in an open platinum dish. It has been my custom, for some time past, to substitute for the dish a large broad weighing bottle, of ordinary form, holding somewhat more than 100 c.c. The vessel being closed after dryness is obtained, the weighing may be done at leisure. Results are more satisfactory, but great difficulty is found in afterwards removing the stopper of the bottle, owing to the high temperature at which it was closed. To overcome this objection, I have had bottles made with a small stop-cock in place of the usual handle on the cover, and am thus able to control the inside pressure. Such bottles may be obtained of Eimer and Amend, New York.—*The Journal of Analytical Chemistry*, January, 1890.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Schäffer's Betanaphthol - betasulphonic Acid—As no answer has appeared to the query in the issue for March 14th, as to the mode of preparing this substance, I may quote the following passages from "Commercial Organic Analysis," vol. iii., p. 194:—"When betanaphthol is heated with twice its weight of strong sulphuric acid (sp. gr. 1.845) to about 90° C., until completely sulphated, the chief product is a monosulphonic acid, known as 'Schäffer's acid.' When betanaphthol is added gradually to twice its weight of strong sulphuric acid (sp. gr. 1.845), taking care that the temperature does not rise above 50° to 60° C., Schäffer's acid, and an isomeric acid, betanaphthol-alphasulphonic acid, often known as Bayer's acid, are formed in about equal quantity. The use of a temperature of 20° C. for preparing Bayer's acid has been patented. Schäffer's and Bayer's acids may be separated by converting them into sodium salts and treating the dry product with alcohol, in which liquid the salt of betanaphthol-alphasulphonic is by far the most readily soluble. Another method of separating Bayer's acid from Schäffer's and another isomeric acid said to be present, is based on the different facility with which the three acids act on certain azo-compounds. Thus, by treating the alkaline solution of the mixed sulphonic acids with a properly regulated quantity of tetra-azo-diphenyl, the unnamed acid and Schäffer's acid are precipitated as claret-coloured dyes, while Bayer's acid remains in solution in the requisite purity for the manufacture of crocein scarlet, for which purpose the isomeric acids are not available. A naphthol-sulphonic acid distinct from, and giving shades redder than either of the above acids, is said to be obtainable by a process described in patent No. 15,781, of 1885." The sulphonic acids of alphanaphthol have been recently described by F. Bender (*Ber.*, xxii., 993).—ALFRED H. ALLEN.

ERRATUM.—P. 169, in the paragraph headed "Filtering-Paper from Grycksbo, Sweden," for "The acid and the water extract from this paper," &c., read "The acid and the water extract nothing from this paper," &c.

MEETINGS FOR THE WEEK.

- MONDAY 21st.—Medical, 8.30.
Society of Chemical Industry, 8. "On the Expulsion of Ammoniacal Compounds from Sulphuric Acid used in Kjeldahl Determinations," by Dr. Moritz. "The Petroleum Fields of India," by Boretton Redwood.
- TUESDAY, 22nd.—Society of Arts, 5. "The Danube and its Trade," by Sir John Stokes, K.C.B.
Royal Institution, 3. "The Place of Oxford University in English History," by The Hon. George C. Brodrick, D.C.L.
Royal Medical and Chirurgical, 8.30.
Institute of Civil Engineers, 8.
- WEDNESDAY, 23rd.—Society of Arts, 8. "Coal in the South-East of England," by William Whitaker, F.R.S.
- THURSDAY, 24th.—Royal Institution, 3. "The Heat of the Moon and Stars" (the Tyndall Lectures), by Prof. C. V. Boys, A.R.S.M., F.R.S.
Royal, 4.30.
Institute of Electrical Engineers, 8.
- FRIDAY, 25th.—Royal Institution, 9. "The Shape of Leaves and Cotyledons," by Sir John Lubbock, D.C.L., F.R.S.
Quekett Club, 8.
- SATURDAY, 26th.—Royal Institution, 3. "Colour and its Chemical Action," by Captain W. de W. Abney, F.R.S., &c.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1587.

ANALYTICAL TOUTS.

THE *City Leader* has lately been calling attention most emphatically to a scandal in the analytical profession. It appears that letters are being sent out to manufacturers, offering to submit their products to a careful analysis, and to embody the results in a "pithy and concise report," which, the recipient is told, "if printed on your circulars, labels, and show-cards," will be found "productive of excellent business results."

The issue of such letters by a person calling himself "F.C.S." our contemporary thinks scarcely in keeping with the dignity of a scientific body, and he is undoubtedly right.

But he asks further, in a later issue, whether the writer is really a Fellow of the Chemical Society or not, adding that "if he is, he should certainly take steps to have his name included in the list." He also expresses himself "somewhat surprised that the Chemical Society has not taken some notice of the matter." Here our contemporary is at fault. The silence of the Society is due, not to approval or indifference, but to want of powers. If Tom, Dick, or "Arry" thinks proper falsely to call himself a Fellow of the Chemical Society, there appears to be no remedy! The other chartered societies are in the same position. Hence it is suggested that they should join hands and endeavour to obtain the power to restrain any illicit assumption of their distinguishing titles.

The same bodies are also, it appears, in want of the power to eliminate any Fellow who acts in a manner calculated to bring the Society to which he belongs into contempt. A Fellow of the Chemical Society, indeed, on his reception, formally pledges himself to uphold the dignity of the Society. But it is very doubtful if this provision would enable the Council to get rid of an undesirable Fellow.

We must further point out that the Chemical Society, unlike the Institute of Chemistry, the Pharmaceutical Society, or the Royal College of Surgeons, &c., is not a professional organisation. This difference materially affects its powers of dealing with undesirable subjects. If any man calls himself, falsely, a member of the Pharmaceutical Society, the Courts make short work of him. But before bogus Fellows of any non-professional Society, such as the Royal, the Linnean, the Chemical, or the Geological, can be made to lay aside their borrowed plumes the law will have to be altered.

Dr. H. E. Armstrong, F.R.S., and Mr. J. M. Thomson, F.R.S.E., the Secretaries of the Chemical Society, have both written to the editor of the *City Leader*, assuring him that the person referred to in the articles of March 29 and April 12 is not a Fellow of the Chemical Society. An official letter has also been sent to the individual in question, informing him that, not being a Fellow of the Society, he is not justified in appending to his name the letters F.C.S. This caution, it is important to note, was given prior to the date of his circular quoted in the *City Leader*. Hence he can scarcely be supposed to have assumed the title in mistake.

As he declares himself to be also a Fellow of the German Chemical Society, it might be well to address an inquiry to the Secretary of that distinguished body at 35, Georgenstrasse, Berlin, N.W.

Preparation of Litmus-Paper.—E. Utescher (*Apotheker Zeit. per Chem. Industrie*) recommends hydrochloric acid instead of phosphoric acid.

VOLUMETRIC DETERMINATION OF TANNIN.

By E. GUENEZ.

THE process of Löwenthal, modified by Neubauer, the most important of the volumetric methods, is applicable only in certain cases. It is founded upon the oxidation of tannin by permanganate, and it can be accurate only if applied to a solution of pure tannin. The presence of organic matters which accompany tannin in industrial extracts becomes a grave source of error.

The author finds a rapid process for the determination of tannin upon the following reactions:—

1. If into a boiling solution of potassium-antimony tartrate, mixed with a suitable aniline colour, there is poured a solution of tannin, there is formed a precipitate of antimony tartrate, which carries down the colouring-matter, forming a true lake. If the proportion of tannin is sufficient, the supernatant liquid becomes colourless. The antimony salt must be in excess in reference to the colouring-matter.

2. The volume of the coloured solution of the antimony salt, and the volume of the solution of tannin which must be added, are always proportional. Dilution does not affect the results.

3. A given quantity of antimony tannate always fixes the same quantity of colouring-matter.

4. If a solution of gallic acid is poured into a boiling solution of the antimony salt, no immediate precipitate of antimony gallate is formed. Under the same conditions, the antimony tannate is produced immediately. Hence it is permissible to suppose that the presence of gallic acid does not interfere.

The method of operating is as follows:—

A solution is prepared of—

Antimony salt	..	..	..	12 grms.
Poirier's green, 4JE	..	..	..	1 grm.
Distilled water	..	..	..	1 litre

The antimony salt and the colouring-matter are dissolved separately; the two solutions are then mixed and filtered. The aniline greens are the only colours suitable, and Poirier's green, 4JE, has given excellent results. This solution is standardised by means of a solution of tannin in ether, perfectly pure and dried previously in a vacuum over sulphuric acid. A solution is made up containing 5 to 6 grms. per litre, and there is added a small quantity of thymol, dissolved in alcohol to prevent mouldiness.

A burette, fitted with a glass cock, is filled with a solution of tannin, and, on the other hand, 20 c.c. of the coloured solution of antimony salt and an equal volume of distilled water are put in a glass tube 35 c.m. in diameter. The coloured solution is raised to a boil, and the tannin liquid is run in, at first by c.c., and afterwards by drops, until the complete decolouration of the liquid, which must be boiled anew after each addition of tannin. There is formed a green flocculent precipitate, which readily collects together, and enables the decolouration of the liquid to be observed. When complete, the volume of the tannin consumed is read off on the burette, and the standard of the antimony solution is thus known.

This method is readily applicable to the analysis of industrial extracts, but as the tannins of these extracts are not identical with the tannins of gall-nuts, which has been selected as a standard, the richness of an extract will be represented in the analysis by an equivalent weight of nut-gall tannin.

This is the case with all volumetric processes, when it is not possible to titrate the liquid with the same kind of tannin which has to be determined. The process of Muntz may be utilised to find the agreement between the gravimetric and the volumetric determination. The process is not vitiated by the presence of gallic acid, but it is not applicable to the determination of tannin in wines.—*Comptes Rendus*, cx., p. 532.

EXAMINATION OF CORPSES FOR ALKALOIDS
AND OTHER NITROGENOUS BASES.

By Dr. ANTON SEYDA.

(Continued from p. 185).

IV. Examination for Metallic Poisons.

For this purpose we use either the matter remaining after extraction with alcohol or the residue from distillation. In the former case the residual alcohol present must be removed by heat; the residue is then stirred up with hot water and potassium chlorate in a porcelain capsule, and chlorinised by the fractional addition of hydrochloric acid until the organic tissue is totally destroyed and all the potassium chlorate is decomposed. The uniform paste thus obtained is heated until all chlorine is driven off, during which any excessive concentration of the hydrochloric solution is obviated by the repeated addition of water as it evaporates. Jeserich's suggestion for the use of chloric acid cannot be acted upon, as the author has never been able to procure it free from arsenic, even 50 c.c. yielding a distinct arsenical mirror.

The thin paste is then placed entirely in a beaker, mixed with tartaric acid to dissolve all the antimony present, strongly diluted with water, and set aside for twenty-four hours.

A. Examination of the Portion Insoluble in
Hydrochloric Acid.

The undissolved residue is filtered off and washed until the washings run through colourless. If the residue is large it should be once more submitted to treatment with potassium chlorate and hydrochloric acid, and dehydrated with alcohol, which is again expelled by ether. For the better extraction of the fat the precipitate is taken from the filter, placed in a beaker, and digested with ether until a fresh portion of the solvent remains colourless. The residue, after the removal of the fat, is then incinerated in a porcelain crucible. The ash is extracted with water containing hydrochloric acid (since it may contain alkaline and earthy-alkaline phosphates and carbonates), and the residue, after being well washed upon a filter free from ash, must be ignited together with the filter in a tared porcelain crucible and weighed when cold.

If the residue does not consist of quartz-sand (fine or coarse) it must be opened up by fusion in a platinum crucible with sodium carbonate (free from alumina and silica). When cold the melt is lixiviated and the lye is let stand in a beaker until clear. Any sediment is filtered off, dissolved in nitric acid, and the solution tested with ammonia, hydrochloric acid (silver), sulphuric acid (lead, barium, strontium), and sulphuretted hydrogen. The filtrate is acidified with hydrochloric acid and evaporated to dryness; the residue dried at 110°, moistened with hydrochloric acid, and taken up in water. Insoluble flocks consist of silica; the solution is tested for sulphuric acid and alumina. In most cases the portion insoluble in chlorine or hydrochloric acid consists of sand, silica, or aluminium silicate. In a notorious case of poisoning with barium chloride, the author found in the residue 0.158 grm. barium sulphate. It occurred only in the contents of one vessel in which had been placed the large abdominal glands, parts of the heart and of the lungs, weighing in all 719 grms. In the lot containing the stomach, the cesophagus, and the duodenum, no barium was present. As it appeared from the evidence, the bulk of the barium chloride had been already expelled by means of Glauber's salts. The barium could neither be extracted from the organs of the corpse by digestion with water nor in hydrochloric acid, consequently it must have been already converted into sulphate in the system,

B. Examination of the Portion Soluble in
Hydrochloric Acid.

The brownish filtrate, freed from chloric acid and chlorine and mixed with the washing-waters, is measured or made up to a known volume (300—500 c.c.). For the process to be followed, the absolute absence of chlorine and chloric acid is essential, a point which must be ascertained by well-known check-reactions with zinc iodide starch paste, or sulphindigotic acid and sodium sulphite. First comes the—

a. Examination for Mercury, Antimony, and Arsenic.

a. Detection and Determination of Mercury. — (The qualitative process is a modification of that of Ludwig and Fürhinger). 50 to 100 c.c. of the liquid are placed in a porcelain dish and neutralised with potassa-lye until the reaction is faintly acid. It is then digested on the water-bath at about 70° for fifteen minutes along with a little bright brass wool. The latter is then taken out, rinsed with water, alcohol, and ether, dried in the exsiccator, and introduced into a tube of sparingly fusible glass charged with granulated copper oxide and drawn out into a narrow end with two prominences. The tube is laid in a combustion furnace, the one end is connected with a Woulff's bottle containing strong sulphuric acid, whilst the capillary end is joined to an aspirator. The copper oxide is first heated, then (whilst a slow current of air is drawn through) that part of the tube where the brass-wool lies is gradually heated and finally raised to redness. After half an hour the heating is stopped, the tube, whilst still hot, is fractured at its point of contraction by means of a drop of water, and the capillary is examined with the naked eye, or with a lens for a mercurial ring. Then, whether mercury globules have been detected or not, a small fragment of iodine is introduced into the capillary at its fractured end, and a current of air or of iodine vapour is drawn through with the application of heat. If the smallest quantity of mercury is present, there appears at the spot a red coating of mercuric iodide, which, on heating, turns yellow and resumes its scarlet colour on cooling.

(To be continued).

NOTE ON A DECA-HYDRATED ACETATE OF
LEAD.

By A. E. FASNACHT and C. R. LINDSEY, B.Sc.

DURING the winter of 1888-9 we found on two occasions crystals that, from their mode of occurrence, were at first thought to be a basic acetate of lead, but which proved on examination to be the normal salt, but crystallised with ten equivalents of water instead of with three. The best crystals were formed on some bristles from a sweeping brush, and were about half an inch long, complete in all their forms; but most of them were implanted by one end. At first they were colourless and transparent, but gradually became opaque, passing ultimately into a milk-white. An analysis shewed—

Pb	40.60	
C ₂ H ₃ O ₂ ..	23.19	by phosphoric acid distillation.
H ₂ O	36.21	by difference.

100.00

While the calculated percentage of Pb(C₂H₃O₂)₂ + 10H₂O gives—

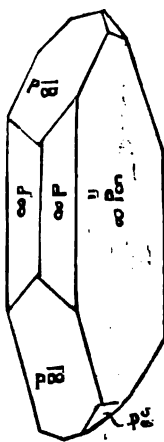
Pb	40.98
C ₂ H ₃ O ₂ ..	23.37
H ₂ O	35.65

100.00

The slight difference is no doubt due to the crystals not being perfectly dry; 40.60 of Pb as found requires, ac-

according to calculation, 23.15 of $C_2H_5O_2$, which agrees very closely.

The specific gravity as determined in petroleum is 1.689 , and the melting-point $72^\circ F.$ This very low melting-point prevented exact determinations of the crystalline form, as the crystals could not be handled without seriously affecting the reflections from their faces. The comparison of a considerable number of measurements, executed as carefully as possible, appears to leave no doubt that the crystals are rhombic, of the form shown in the figure, in which—



$$\infty P = 110^\circ.$$

$$P\infty = 75 \text{ (over summit).}$$

$$\infty P\infty : P\infty = 90^\circ.$$

These are the most accurately measurable, and are certainly correct within a few minutes.

$$P\infty = 95^\circ 20' \text{ (over summit).}$$

$$\infty P\infty : P\infty = 132^\circ 20'.$$

$$\infty P : P\infty = 130^\circ 20' \text{ (calculated } 130^\circ 28').$$

$$\infty P\infty : \infty P = 125^\circ.$$

These give an axial ratio of—

$$\text{brachy} : \text{macro} : \text{prin.} = 0.7002 : 1 : 0.9125.$$

The ordinary crystals with three of water are monoclinic.

Clayton, Manchester,
March 28, 1890.

THE SPONTANEOUS IGNITION OF COAL CARGOES.*

By Professor VIVIAN B. LEWES,
Associate of the Institution of Naval Architects, F.C.S., F.I.C.
(Concluded from p. 188).

(7) Rise in temperature in steam colliers due to the introduction of triple expansion engines and high-pressure boilers.

It has been fully pointed out that anything which tends to increase of initial temperature increases the rapidity of chemical action. Steam at 80 lbs. boiler pressure has a temperature of $324^\circ F.$ ($162^\circ C.$), and a common stokehold temperature with boilers worked at this pressure is 100° to $130^\circ F.$ (or 38° to $54^\circ C.$). Steam at a boiler pressure of 155 lbs. has a temperature of $368^\circ F.$, or $186^\circ C.$, and gives a corresponding increase of temperature in the

TEMPERATURE RECORDS. H.M.S. Malabar and Crocodile. Crocodile (original simple low-pressure engines).

Locality.	Date.	Deck.	Coal bunkers.	Engine room.	Stokehold.
1874.					
Channel and Bay	Jan. 15	52	72	98	90
" "	" 18	58	80	99	92
Mediterranean ..	" 23	65	86	98	92
" "	" 27	66	84	190	92
Red Sea	Feb. 6	68	92	108	106
"	" 10	81	100*	114	110
1875.					
Channel and Bay	Feb. 11	46	66	90	105
" "	" 12	54	70	94	102
Mediterranean ..	" 19	53	74	92	89
" "	" 26	66	74	98	104
Red Sea	Mar. 4	77	90	104	115
"	" 6	82	94	98	120
Indian Ocean ..	" 12	79	98*	104	114

Malabar (old compound engines).

1885.					
Channel and Bay	Oct. 3	59	85	82	89
" "	" 6	63	86	86	110
Mediterranean ..	" 8	72	90	98	94
" "	" 9	73	90	96	100
" "	" 10	70	90	90	110
Red Sea	" 19	81	92	95	107
"	" 20	84	100	96	108
"	" 21	88	104*	104	119
"	" 23	87	102	97	112

Crocodile (compound engines).

1888.					
Channel and Bay	Dec. 4	55	78	78	90
" "	" 6	54	85	80	84
" "	" 8	60	92	82	88
Mediterranean ..	" 12	64	97	80	100
" "	" 15	60	95	78	90
" "	" 17	62	112	83	94
Red Sea	" 22	74	113	92	100
"	" 23	80	115	96	103
"	" 24	82	116*	98	110
Indian Ocean ..	" 31	78	99	97	118

Malabar (new triple engines).

1888.					
Channel and Bay	Dec. 13	49	77	78	72
" "	" 14	56	86	86	88
" "	" 16	62	80	84	90
Mediterranean ..	" 18	63	88	90	94
" "	" 19	62	88	90	94
" "	" 22	68	87	90	100
" "	" 23	74	89	90	98
Red Sea	" 28	79	96	102	110
"	" 29	82	100	100	110
"	" 30	84	105*	100	108
"	" 31	83	104	104	110

1889.					
Channel and Bay	Oct. 5	65	84	86	94
" "	" 7	67	84	90	102
Mediterranean ..	" 10	76	100	92	102
" "	" 11	80	100	93	99
" "	" 15	79	104	96	100
" "	" 16	80	106	96	106
Red Sea	" 19	83	106	103	102
"	" 20	86	110	102	110
"	" 21	89	115	108	108
"	" 22	92	120*	112	122

NOTE.—The Registers of the original engines of Malabar are destroyed; temperature records of Crocodile are given in lieu, for a period when she was fitted with old low-pressure engines.

* Read at the Thirty-first Session of the Institution of Naval Architects, March 28, 1890; the Earl of Ravensworth in the Chair.

* Maximum temperature during voyages from Portsmouth to Bombay.

stokehold and other adjacent portions of the vessel, the temperature in the stokehold under these conditions being from 110° F. (43·5° C.) to 140° F. (60°), and increase of about 10° F.

It is, however, difficult in the mercantile marine to get a direct comparison of the increase in temperature due to this cause, but in the service, some of the troopships have been from time to time refitted, and in the case of the *Malabar* and *Crocodile*, the temperatures existing with the old simple low-pressure engines, the old compound engines, and the new triple expansion engines can be contrasted, and will be found in the accompanying Table, for which I am indebted to Mr. White.

From this it will be seen that, taking the voyage throughout, the average increase of temperature in the stokehold from the use of the triple expansion engines is about 5 degrees. This table is of great interest, as the temperatures taken during the outward voyage of the *Crocodile*, December, 1883, point to the coals in the bunkers commencing to heat, and also illustrate where and at what temperature it commenced.

Crossing the Bay, the stokehold and bunker temperatures agree fairly well, but entering the Mediterranean, the stokehold having become heated to 100° F. on the 12th, action commenced in the bunkers, and this rapidly raised their temperature higher than that of the stokehold, the action, however, not being violent, and the bunker temperature rapidly falling below that of the stokehold as the chemical action died away.

Having now discussed the chemical and physical conditions which lead to the phenomenon known as "spontaneous ignition," we can formulate precautions which will tend to prevent such disasters.

1. The Choice of Coal for Shipment to Distant Ports.

The coal should be as large as possible, free from dust, and with as little "smalls" as can be helped.

It is better as free from pyrites as possible, in order to prevent disintegration after shipment, and it should contain when air-dried not more than 3 per cent of moisture.

2. Precautions to be Taken during Shipment.

No coal should be shipped to distant ports until at least a month has elapsed since it was brought to the surface at the pit's mouth. Every precaution should be taken to prevent breaking up of the coal whilst being taken on board, and on no account must any accumulation of fine coal be allowed under the hatchways.

When possible the coal should be shipped dry, as external wet, by producing oxidation of the pyrites, causes disintegration.

3. Precautions to be Taken on Board Coal-laden Ships.

This phase of the question is undoubtedly the most important, and in order to ensure any successful treatment of the coal cargo at sea to prevent undue heating and ignition, the means adopted must be as nearly automatic in their working as possible, as it is useless to expect the master or any officer on board a collier during rough weather, &c., to comply with any instructions, such as daily taking the temperatures in various parts of the cargo, and so on.

The coal compartments should be made gas-tight, as far as the bulkheads separating them from the rest of the ship is concerned; and as no difficulty is found in doing this when provision for forced draught is being made, no difficulty should be found in this case.

When the coal has all been taken in, it should be battened down, and the hatches should not be again opened until the vessel reaches her destination, the only ventilation allowable being a 2-inch pipe just inserted into the crown of each coal compartment, and led 12 feet up the nearest mast, the top being left open. This would be quite sufficient to allow free egress to any gases evolved by the coals, but would not allow undue access of air.

Into the body of the coal cargo itself would be screwed, at regular intervals of about 6 feet, iron pipes, closed at the bottom, and containing alarm thermometers, constructed in the following way:—A long bulb of glass, containing mercury, has an insulated wire inserted into the quick-silver, and making contact with it, whilst the stem attached to the bulb has a second wire in it, so arranged that when a rise of temperature causes expansion of the mercury, in rising in the tube it makes contact, and the wires from these tubes are in connection with an electric bell, index board, and battery in the captain's room, so that the moment the temperature is reached to which the thermometers have been set, the bell rings, and will continue to ring until the temperature again sinks, the spot in which the heating is taking place being indicated by the index board.

In the evidence given before the Commissioners in 1875, Mr. J. Glover strongly advocated the use of carbon dioxide, or carbonic acid gas as it is more usually termed, for extinguishing ignition when it has broken out in a coal cargo, and for stopping heating when it has reached a dangerous pitch. His proposal was to generate the gas by the action of hydrochloric acid upon chalk, and to lead it by gas pipes to the compartment affected, and this gas, being heavier than air and a non-supporter of combustion, was to displace the air and its contained oxygen, and so to prevent further action by surrounding the coal with an atmosphere which could not carry on combustion. The idea was a good one, but there were many difficulties in the way of carrying it out, one being that for every thousand tons of coal carried, 80 cwt. of hydrochloric acid would have had to be shipped, also the gas could not have been driven down into the hold if any serious heating had taken place, as an up current would have been formed and would have carried it away, whilst in this state of gas it fails to give any great cooling effect, and so would have exercised but little influence upon the mass of red hot fuel. These objections weighed so strongly with the Commissioners that in their final Report we find the following sentences:—

"Several methods for generating carbonic acid gas and applying it to the ignited portion of a coal cargo have been proposed for our consideration. We consider, however, that although this gas might be useful by excluding atmospheric air (which is essential to support combustion), yet it will not, as water does, exert any very sensible cooling effect, which is a point of vital importance in the case of a mass of ignited coal. We are of opinion that water and steam are the only agents practically available for the purpose of extinguishing fire in coal cargoes."

Applied in the way which was suggested there is no doubt but that the carbonic acid gas would have been practically useless; but there is another way in which it could be used, which would make it a most powerful cooling agent, an instantaneous quencher of fire, and would prevent any further tendency to heat on the part of the coal treated with it.

If carbonic acid gas is compressed under a pressure of 36 atmospheres at a temperature of 32° F. (0° C.), it is condensed to the liquid state, and can be obtained in steel vessels closed with screw valves. On opening the valve some of the liquid is ejected into the air, and on coming into the ordinary atmospheric pressure, is in a moment converted into a large volume of gas. Conversion from the liquid to the gaseous state means the absorption of a large amount of heat, and so great is this that everything near the stream of new-born gas is cooled down, and some of the escaping liquid is frozen to a solid, having a temperature of -78° C., or -108·4° F.

This liquid carbonic acid gas is now extensively manufactured, and is used abroad to a large extent for aerating waters, driving torpedoes, and for freezing machines; and I should suggest its use in the following way for the checking of ignition in the coal cargo:—

The nozzle attached to the screw-valve on the bottle of condensed gas would have a short metal nose-piece

screwed on to it, the tube in which would be cast in solid, with an alloy of tin, lead, bismuth, and cadmium, which can be so made as to melt at exactly 200° F. (93° C.). The valve would then be opened, and the steel bottle buried in the coal during the process of loading. The temperature at which the fusible metal plug will melt is well above the temperature which could be reached by any legitimate cause, and would mean that active heating was going on in the coal; and under these conditions the pressure in the steel cylinder would have reached something like 1700 lbs., and the moment the plug melted the whole contents of the bottle would be blown out of it into the surrounding coal, producing a large zone of intense cold, and cooling the whole of the surrounding mass to a comparatively low temperature. The action, moreover, would not stop here, as the cold, heavy gas would remain for some time in contact with the coal, diffusion taking place but slowly through the small exit pipe.

When coal has absorbed as much oxygen as it can, it still retains the power of absorbing a considerable volume of carbonic acid gas; and when coal has heated, and then been rapidly quenched, the amount of gas so absorbed is very large indeed, and the inert gas so taken up remains in the pores of the coal, and prevents any further tendency to heating; indeed, a coal which has once heated, if only to a slight degree, and has then cooled down, is perfectly harmless, and will not heat a second time. It is not by any means necessary to replace the whole of the air in the interstices of the coal with the gas, as a long series of experiments show that 60 per cent of carbonic acid gas prevents the ignition of the most pyrophoric substances.

One hundred cubic feet of gas can be condensed in the liquid state in a steel cylinder 1 foot long and three inches diameter, and it has been shown that a ton of coal contains air spaces equal to about 12 cubic feet; therefore, one of these cylinders would have to be put in for every 8 tons of coal, and these would be distributed evenly throughout the cargo, and near the alarm thermometers, which would be set to ring a degree or two below the point at which the fusible plug would melt.

The bell ringing in the captain's room would warn him that heating was taking place, and the bell would continue to ring until the cylinder had discharged its contents, and had cooled down to a safe degree, so that the whole arrangement would be purely automatic, and yet the officers would know if everything was safe.

This liquid is now being made at a comparatively cheap rate, and with any demand for its machinery could be put up at the principal coaling ports to charge empty cylinders at a very low rate, so that the initial cost of the steel cylinders once got over the expenses would not be worth considering, more especially as one, or two at most, would be likely to go off.

If the precautions advocated were taken no danger could arise until the arrival of the ship at her destination, and the commonest precautions would then suffice. On removing the hatches, no naked light must be allowed near them, and no one must be allowed to descend into the hold until all the gases have had time to diffuse out into air. If the cylinders have gone off there will be but little fear of explosion, as a high percentage of the carbonic acid gas lowers the explosive power which the mixture of marsh gas (given off from some coals) and air possess; but the carbonic acid gas would overcome and suffocate a man descending into an atmosphere containing any considerable percentage of it. When a safety lamp, lowered into the hold, continues to burn as brightly as it did in the open air, then it is perfectly safe to descend.

When once coal in a cargo has fired, pumping in water is of practically no use, as the fire is, as a rule, near the bottom of the mass of coal, and the flow of the water is so impeded, that in percolating through the interstices of the heated coal, it is converted into steam before it can reach the seat of combustion. The most effective way to apply

water would be to have four 3-inch pipes laid along the floor of the coal compartments, about 6 feet apart, these tubes having a $\frac{1}{2}$ -inch hole bored in the upper side every foot or so, and each pair of pipes coming through the bulkhead, and connecting on to two 6-inch pipes passing through the side of the vessel, the sea water being prevented from entering by means of screw valves. As soon as the alarm thermometer gave notice that heating had reached a dangerous point, these valves could be opened and the lower portion of the cargo drenched with salt water. This, evaporating rapidly, would give large volumes of water vapour, which, passing up through the heated coal, would lower its temperature, but would not be nearly as effective as the method before advocated. It might, however, be used in conjunction with that method, and would, in many cases, save the carbonic acid gas.

The question of preventing the heating and ignition of stores of coal on land and ready for use in bunkers, cannot be met so well by the use of the liquid gas, and, in these cases, it would be found beneficial to dress the coals with a little tar or tar oil, which would close the pores, and to a great extent prevent oxidation. I believe this was advocated by Lachman about 1870.

Crude petroleum in small quantities for this purpose would also be found valuable, for, as already shown, it has no tendency to oxidise itself, and lowers the tendency in other bodies, besides coating them, and so preventing access of oxygen.

The labour trouble in the coal trade is hampering all branches of industry, and, with increasing difficulty in obtaining coal, all sorts of rubbish will be shipped, and many a cargo of coal will go out during the next few months which, under normal conditions, would never have been allowed on board: and we may expect a heavy increase in the loss of life and property from spontaneous ignition. This will probably result in a rise in the rate of premium, and further check to our export coal trade; and I sincerely trust that, should these gloomy forebodings be fulfilled, the suggestions made in this paper, and based on experimental facts, may be found of value.

In conclusion, I wish to acknowledge my indebtedness to the researches of Dr. Richters, whose papers on the weathering of coal are to be found in Dingler's *Polytechnisches Journal* for 1870; to the Report of the Royal Commissioners on this question in 1876; and, finally, to Mr. Martell for suggesting the subject of this paper.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, April 5th, 1890.

SIR,—We submit herewith the results of our analyses of the 177 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 1st to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 177 samples examined were found to be clear, bright, and well filtered.

Throughout the month of March the condition of the water furnished to the Metropolis by the Companies taking their supply from the Thames and the Lea has continued to be unexceptionable. The mean proportion of organic carbon present in the Thames-derived samples having been found to be 0.154 part in 100,000 parts of the water, as against a mean of 0.160 part in the previous month's supply.

During the first three months of the year we have examined a total of 534 samples. With the exception of two of the February samples recorded as being "very slightly turbid," the whole were found to be clear, bright, and well-filtered. As regards the Thames-derived water, the maximum proportion of organic carbon present in any single sample examined was 0.174 part in 100,000 parts of the water, the mean proportion for the three months being 0.150 part, an exceptionally low result for the first quarter of the year, in which the mean is habitually liable to elevation by reason chiefly of the occurrence of more or less heavy floods, often, indeed, of a succession of floods. It is to be noted, however, that of late years the influence of a flooded state of the rivers upon the character of the water supply is appreciably less than it used to be formerly.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

April 3, 1890.

Dr. HUGO MÜLLER, F.R.S., Vice-President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Robert Appleyard, University College, Dundee; William Henry Blake, 31, Norfolk Street, Sunderland; George Caird, 20, Springfield, Dundee; S. Sydney Monckton Copeman, M.A., M.B., Cantab., 134, York Road, S.E.; Andrew Fairgreve, Sydney, New South Wales; G. H. Findlay, Hawthorn Cottage, Francis Road, Edgbaston, Birmingham; George German, junior, Huntingdon House, Ashby de-la-Zouch; John Archyll Jones, 3, Jedburgh Street, Middlesbrough; Oliver Kirk, Science Schools, South Kensington; Robert Waller Oddy, Waterhouse, Toad Lane, Rochdale.

The following papers were read:—

24. "Note on the Hydrosulphides." By S. E. LINDER and HAROLD PICTON.

The authors find that freshly precipitated metallic sulphides almost always contain hydrogen sulphide; that they are, in fact, hydrosulphides, or the remnants of hydrosulphides; and that if, instead of adopting the usual plan of passing gas through the solution, the metallic salt be allowed to run slowly into a solution of hydrogen sulphide in water in absence of too large an excess of acid, a solution is obtained which can in most cases be freed from dissolved hydrogen sulphide by a current of hydrogen, although this to some extent depends on the character of the acid liberated from the salt. The solu-

tions so obtained are readily precipitated by the addition of metallic salts, a fact long made use of in washing a sulphide such as that of tin, in which case the addition of sodium chloride to the water is always advised.

A large number of experiments on the formation and properties of the metallic hydrosulphides have been made, and, although the work is not yet completed, it is thought to be desirable to indicate generally, and with the aid of two typical examples, the character of the results obtained.

To prepare the higher hydrosulphides, it is found to be necessary to avoid the presence of acid. An unexpected method of accomplishing this has presented itself in certain cases—in that of mercury, for example. If carefully washed mercuric sulphide be treated with hydrogen sulphide and water, it dissolves to a clear brown solution from which uncombined hydrogen sulphide may be removed by a current of hydrogen. Another method which it is hoped will be generally applicable is the treatment of the metallic hydroxides with hydrogen sulphide. Precipitation with sodium hydrosulphide or ammonium hydrosulphide may be resorted to in some cases. By whatever method they are prepared, the hydrosulphides are probably in all cases compounds of high molecular weight. The effect of acids on their formation and constitution is of much interest, as these apparently cause a molecular condensation and increase of complexity, which becomes more marked as the acids become more powerful. Variation in temperature does not appear to exercise any important influence.

The sulphur in the hydrosulphide has been determined as sulphate after oxidation with chlorine, great care having been taken to avoid the precipitation of sulphur during the formation of the sulphide; to make assurance on this matter doubly sure, the authors have in some cases heated the carefully washed sulphate in a current of hydrogen freed from every trace of hydrogen sulphide, the hydrogen sulphide lost on heating being absorbed by potash and oxidised. This method is of special importance as affording confirmation when the combined hydrogen sulphide, as in the case of mercury, is very small in amount.

Copper.—On treating copper hydrate suspended in water with hydrogen sulphide, the hydrosulphide $7\text{CuS}\cdot\text{H}_2\text{S}$ is rapidly formed, and if left for some days in a tightly stoppered vessel, dissolves to a clear brown solution. The effect is the same whether time be given for the solution to form or not. Three results differing from the mean by only about 0.07 in the percentage of sulphur gave as a mean 36.69 per cent of sulphur, the amount calculated for $7\text{CuS}\cdot\text{H}_2\text{S}$ being 36.59 per cent.

In order to prevent the liberation of sulphuric acid during the interaction, sodic acetate was added to the copper sulphate, and the solution formed by adding the mixture to water saturated with hydrogen sulphide was precipitated with ammoniac chloride: two molecular proportions of acetic acid were present for each molecular proportion of CuS . In this case the acetic acid acts in presence of excess of hydrogen sulphide, and has but little effect in breaking down the hydrosulphide. The percentage of sulphur found as 36.00; that calculated for $9\text{CuS}\cdot\text{H}_2\text{S}$ is 35.96 per cent.

In two experiments in which some acetic acid was present at starting, a precipitate was gradually deposited, which was filtered off without adding salt; great difficulty was experienced in effecting filtration owing to the fine state of division of the sulphide. Slightly higher numbers were obtained, probably owing to the deposition of some sulphur, but they serve to indicate that the salt does not alter the composition of the precipitate; the percentages of sulphur found were (1) 36.13, (2) 36.28.

In another case, after adding sodic acetate, the excess of hydrogen sulphide was expelled from the solution of the hydrosulphide by hydrogen. The acetic acid was thus allowed to act upon the solution unsaturated with hydric sulphide. The percentage of sulphur found was

34.67 and 34.56; that calculated for $22\text{CuS} \cdot \text{H}_2\text{S}$ is 34.61. In this case the excess of sulphur is very small, and it is impossible to assign a formula; it is noticeable that a great molecular condensation has taken place.

In presence of hydrogen chloride, still further loss of sulphuretted hydrogen occurs. All the filtrations were conducted in an atmosphere of hydrogen.

Mercury.—Solutions of two similar quantities of mercuric chloride were taken; after boiling to expel air, one was run into boiled water containing hydrogen sulphide placed in a Drechsel's bottle, access of air being prevented by a current of the gas; the mixture was precipitated by hydrogen chloride. The other, after dilution with boiled water, was made acid and precipitated by hydrogen sulphide. Both precipitates were washed with boiled water, then mixed with boiled water in a Drechsel bottle, and hydrogen sulphide was passed into the liquid till clear solutions were formed. A current of hydrogen was then passed through both (the one being cooled with ice) till they were free from hydrogen sulphide. The amount of barium sulphate obtained from A was 0.8910, from B 0.8916; the amount afforded by the same weight of mercuric sulphide is 0.86375. The mean percentage of sulphur found was 14.166; a compound of the formula $3\text{HgS} \cdot \text{H}_2\text{S}$ would contain 14.171 per cent.

In presence of hydrogen chloride a further molecular condensation takes place, the quantity of attached hydrogen sulphide becoming apparently halved; it is of course impossible to assign an exact formula to a product of so high a molecular weight, but the concordance of the results and its very remarkable stability would make it probable that the compound is a definite one. It withstood extraction with carbon disulphide, and the prolonged washing which this entailed. It did not lose its hydrogen sulphide *in vacuo*, and after drying *in vacuo* it required to be heated for about sixteen hours at 105° in a current of hydrogen before all the hydrogen sulphide was removed. The dryness of the hydrosulphide seems to greatly influence the rapidity with which it loses hydrogen sulphide.

25. "Researches on the Germination of Some of the Gramineæ." Part I. By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D.

This investigation was undertaken with the view of throwing some light upon the complex metabolic processes which take place during the germination of seeds. The authors, during the progress of the inquiry, have examined and experimented with the seeds of a great number of the grasses, but this, the first part of their paper, is confined almost entirely to a consideration of the changes which take place in *barley* during the early periods of its growth.

The paper is divided into 21 sections, the heads of which are as follows:—

(1). Introduction. (2). Structure of a grain of barley. (3). The visible changes which occur in the embryo and endosperm during germination. (4). The relation of the embryo to the endosperm. (5). Development of excised embryos upon foreign endosperms. (6). The endosperm to be regarded as a storehouse of *dead* reserve material; no residue of vitality recognisable in its cells. (7). Cultivation of excised embryos upon water. (8). Cultivation of excised embryos upon nutrient solutions. (9). Growth of excised embryos upon *starch*, and proof that an amylolytic (diastase) is secreted by the growing embryo. (10). The secretion of diastase is localised in the "absorptive epithelium." (11). The secretion of diastase is increased by the presence of a small quantity of acid. (12). The secretion of diastase not stimulated by the presence of starch. (13). The secretion of diastase is inhibited by a readily assimilable carbohydrate. (14). The existence of a *cellulose-dissolving* enzyme (cyto-hydrolyst) in the germinating seeds of the grasses. (15). The cyto-hydrolyst, like diastase, is secreted by the "absorptive epithelium." (16). The two varieties of diastase, their genesis and distribution in the resting and germinating seed. (17). Distribution of diastase in the germinating

seed. (18). The "mother-substance" of the "diastase of secretion" is principally derived from the endosperm. (19). Action of "diastase of secretion" upon ungelatinised starch. (20). A consideration of the origin of the hydrolytic enzymes of germinated grain. (21). The form in which the reserve starch after transformation enters the growing embryo, and the metabolic changes which it there undergoes.

In recording the visible changes which occur in the seed during germination, it is shown that a disintegration and dissolution of the cell-walls of the endosperm always precede any attack upon the cell contents. This breaking down of the cell-wall is shown in a subsequent portion of the paper to depend on the production during germination of a special cellulose-dissolving, or "cyto-hydrolytic enzyme," which, like diastase, is soluble. The action of this enzyme on the cell-walls of some kind of vegetable parenchyma is very energetic. The physiological importance of this cyto-hydrolyst is very great, for, owing to the non-diffusible nature of the amylolytic enzyme, diastase, the previous breaking down of the cell-wall is a necessary prelude to the dissolution of the contained starch-granules.

The authors show that the appearance of the cyto- and amylolytic enzymes is due to a specialised secretory function of the layer of columnar epithelium which covers the outer surface of the scutellum. It has hitherto been considered that the function of this epithelium was exclusively that of an absorptive tissue: its absorptive as compared with its secretory functions are, however, of quite secondary importance.

The natural food material, *starch*, does not appear to have any special power of stimulating the cells of the epithelium to increased secretion of a diastase, but the flow both of diastase and of the cyto-hydrolytic enzyme from these cells is affected in a very remarkable manner by the presence of certain carbohydrates. Providing the carbohydrate is one which is readily assimilable by the embryo, such as cane-sugar or maltose, secretion of ferment is checked or even entirely inhibited. No such inhibitory action is, however, produced by such substances as mannitol and milk-sugar, which are entirely without nutritive value. The authors' experiments in this direction point to the secretion of the amylolytic and cyto-hydrolytic enzymes as being to some extent *starvation phenomena*. The power of secretion possessed by the epithelium is in some way or other so adapted to the requirements of the young plants as to be only exercised when the supply of tissue-forming carbon compounds begins to fail.

The histological changes which take place in the cells of the epithelium during secretion are very similar to those which have been observed in certain secretory cells of the alimentary tract of animals, and in the secretory cells of some of the insectivorous plants.

The authors confirm the important generalisation of Sachs that the relation of the embryo to the endosperm is that of parasite to host, and they have availed themselves of this relation by cultivating the embryo upon suitable media after separating it from its endosperm, and in this way they have obtained information with regard to the secretory powers of the embryo, and the chemical modifications of its absorbed nutriment, which it would have been impossible to obtain by any other means.

The results of cultivating excised embryos upon various nutrient solutions, more especially of the carbohydrates, are recorded, and it is shown that whilst cane-sugar, invert-sugar, dextrose, lævulose, maltose, raffinose, galactose, and glycerol have all more or less nutritive value, milk-sugar and mannitol do not in any way contribute to the growth of tissue in the young plant. Of all substances tried, cane-sugar has by far the greatest nutritive power. Maltose, although the natural food of the embryo when attached to its endosperm, is decidedly inferior in this respect to cane-sugar. This, at a later point in the paper, is shown to be due to the fact that

maltose, directly it is absorbed by the growing embryo, becomes transformed into cane-sugar by the living cells, and in this form is passed from cell to cell. When cane-sugar is supplied ready formed to the young plantlet, there is manifestly a saving of energy to the living cell, which receives its nutriment in a form in which it is directly available for its requirements.

An examination of the sugars produced during the germination, and of their mode of distribution in the grain, have convinced the authors that the transformed starch of the endosperm is absorbed by the embryo in the form of maltose, and that the seat of production of the cane-sugar which germinated grain contains is the tissues of the embryo itself.

The authors are continuing their work upon the germination of the grasses, and are applying the methods described in this first part of their paper to an elucidation of the chemical changes which the other reserve materials, especially the proteids, undergo in their passage from the endosperm, and of the agencies which are at work in bringing about these transformations.

DISCUSSION.

Mr. THISELTON DYER said that chemists, perhaps, would hardly realise what delicacy of manipulation was required in carrying out experiments such as had been instituted by the authors of the paper; it was a fortunate circumstance that the morphology of the seed in grasses allows of an anatomical separation of the elements. Botanists had already made some progress in localising enzymes: thus Professor Marshall Ward had shown that the enzyme which effects the liberation of the colouring-matter from the glucoside in Persian berries is located in the raphe; and it had long been known that emulsin was not distributed throughout the bitter almond. After referring to the distinction between animals and plants, he said that the plant was similar to the seed, the bud corresponding to the embryo, and the woody shoot to the endosperm. Baranesky had shown that a diastase is omnipresent in plants; and there could be little doubt that it would be found that an enzyme capable of attacking cellulose was equally so.

Professor MARSHALL WARD pointed out that in the seeds of the *Gramineæ*, *Cyperaceæ*, and other families of plants there is a peculiar layer of cells, from one to three or more deep, surrounding the starchy endosperm, and distinguished from the latter by containing no starch but relatively large quantities of proteids: this layer belongs to the endosperm, but as the seed ripens the cells store special proteids instead of the starch-grains which predominate in the other endosperm cells. In the oat there is such a layer, one cell deep, and it has been shown that, during germination, the dissolution of the starch and the cell-walls of the starch-containing cells begins near the surface of this layer, which itself persists, and the cells of which take up food and undergo changes so like those of excreting cells that it was concluded that they excrete the diastatic enzyme. Haberlandt declares that when starch-grains are placed in contact with a piece of this layer kept moist and at proper temperatures, the grains even of the resistant potato-starch are corroded as on germination; whereas control experiments, where all conditions are the same, except the presence of the cells of the proteid layer, showed no such corrosion.

Professor Ward then remarked that the authors' suggestion that more than one enzyme may be excreted according to the nutrition of the cells, and their proof that a cellulose-dissolving enzyme exists in barley, is borne out by various recent researches and by Wortmann's observations on the behaviour of bacteria in a mixture of starch and proteids. Wortmann proved that so long as the bacteria were fed with proteids, they refused to excrete the diastatic enzyme which they produce in abundance when only carbohydrates are at their disposal.

The speaker concluded by drawing attention to several

other cases where such a proteid layer exists—e.g., in the seeds of buckwheat and in the tubers of some potatoes—and remarked on the importance of clearing up this matter, and on the steps towards accomplishing that end attained by the excellent work of the authors of the present paper.

Professor GREEN said that in the case of the date stone his observations led him to believe that the enzyme was independent of the endosperm, and that probably it was located in the epithelial layer, but in castor oil seeds not only the embryo but also the endosperm cells appeared to be possessed of vitality, the fatty matter in the latter undergoing change even when not subject to the action of the embryo; probably the enzyme was present in the form of an enzymogen, as extracts of the seeds were rendered active by acids.

Dr. LAUDER BRUNTON said that it was highly remarkable that in a comparatively highly organised plant the conditions of the embryo was so very similar to that of the embryo in animals: the embryo in both cases appeared to be purely parasitic. In the mammalian embryo proteids are taken up from without, and it is generally assumed that they are assimilated without undergoing much change, but this was by no means certain. Referring to the presence in malt of an enzyme capable of affecting cellulose, he said there was a form of indigestion in which people could not digest cellulose: was it possible to separate the enzyme in question in large quantities?

Dr. ARMSTRONG remarked that many of the results brought forward were highly suggestive from a chemical point of view. The authors came to the conclusion that maltose, which on *a priori* grounds might be regarded as the natural nutriment of a plant, was inferior to cane-sugar, and that in the plant maltose was converted into cane-sugar. Dextrose, according to their observations, did not undergo conversion into cane-sugar, but it gave invert sugar; that is to say, it became partially converted into lævulose, but these constituents of cane-sugar were apparently incapable of interacting. It was known from Emil Fischer's experiments that dextrose could be converted into lævulose, and that maltose was an etheric compound of the acetyl type, formed from two molecules of dextrose, one of which acted as aldehyd, the other as alcohol; it was conceivable that if the "dextrose residue" in maltose underwent a change comparable with that which is involved in the conversion of dextrose into lævulose, a compound would be obtained which, if not identical with cane-sugar, would, perhaps, be easily convertible into cane-sugar by hydration and subsequent dehydration: it is scarcely probable that the keto-group—or its equivalent—of lævulose is preserved in cane-sugar, but if this group were to become $C(OH)_2$ and one of the hydroxyls were to be separated together with an atom of hydrogen of a hydroxyl-group in the other dextrose residue, a more stable etheric compound might result, the properties of which, probably, would be such as are characteristic of cane-sugar. The authors had spoken of the maltose becoming incorporated with the protoplasm, from which the cane-sugar was then elaborated; perhaps the effect was comparable with that exercised by phenylhydrazine in effecting the conversion of dextrose into lævulose through the agency of the osazone.

Dr. Armstrong then took exception to the terms amyolytic, proteolytic, &c., as applied to so-called ferments, pointing out that, whereas the terms electrolysis and hydrolysis implied splitting up by means of electricity and water, amyolytic was intended to suggest the splitting up of starch, proteolytic the splitting of proteids. He suggested several expressions less open to objection.

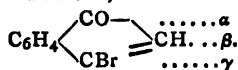
Mr. HERON, referring to the author's conclusion that maltose was not resolved into dextrose during germination, asked how, if this were the case, it was possible to account for the presence of dextrose in malt; he was of opinion that maize diastase did hydrolyse maltose.

Mr. HORACE BROWN said that although, as Mr.

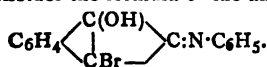
Thiselton Dyer had pointed out, diastase was ubiquitous in plants, that developed during germination appeared to differ in important particulars from ordinary diastase. He had been unsuccessful in isolating an enzyme capable of attacking cellulose from the date stone. Their experiments did not favour the conclusion that the cellulose layer had any marked diastatic power. He might point out that Professor Marshall Ward had been led to a conclusion similar to their own in the case of the cyto-hydrolytic enzyme which he had studied, viz., that its secretion was a starvation phenomenon. All their experiments to determine whether the enzyme existed in the endosperm as an enzymogen had been futile. In preparing the cyto-hydrolytic enzyme from malt, it was necessary to use air-dried malt, as it was destroyed by heating. In his experience there was no marked excess of dextrose in malt.

25. *The Formation of Indene-Derivatives from Dibrom- α -naphthol.* By R. MELDOLA, F.R.S., and F. HUGHES.

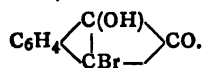
On adding dibrom- α -naphthol to strong nitric acid (1.42 sp. gr.), an oily liquid is first formed, which subsequently solidifies to a mass of crystals, probably consisting of an additive product. If cold fuming nitric acid be used (1.5 sp. gr.), the dibrom- α -naphthol at once dissolves without any evolution of gas, and on pouring the acid solution into water an ochreous precipitate is produced, which, when purified, forms small ochreous scales melting at 127–128°. The substance is regarded by the authors as γ -brom- α -indone,



This compound is converted by the action of aniline into an anilide crystallising in bright red scales melting at 190°. This anilide is acid in character, dissolving in hot aqueous or cold alcoholic soda with a violet colour. The authors consider the formula of the anilide to be—



By boiling with dilute alkali, the anilide is converted into the bromhydroxyindone,—



This latter forms dull orange needles melting at 191°. During the decomposition of the anilide, a strong odour of phenyl-isocyanide is evolved. The barium salt of the bromhydroxyindone forms orange needles of the formula $(\text{C}_9\text{H}_4\text{BrO}_2)_2\text{Ba} \cdot 7\text{H}_2\text{O}$. The aniline salt forms red scales melting at 169° and decomposing at 172°. Other derivatives of the brom-indone, viz., the benzylamide (m.p. 154°) and β -naphthylamide (m.p. about 151°) have been prepared. The authors propose to continue the investigation of these indene-derivatives.

27. *"The Action of Chlorhydric Acid on Manganese Dioxide. Manganese Tetrachloride."* By H. M. VERNON.

In 1821, Forchhammer showed that when the oxides of manganese, MnO_2 , Mn_2O_3 , and Mn_3O_4 , are dissolved in chlorhydric acid, a dark brown solution is formed, which affords a precipitate consisting of a mixture of oxides of manganese when added to a large quantity of water. W. W. Fisher (*Chem. Soc. Trans.*, 1878, 409) showed that this brown solution contained a higher chloride of manganese, probably the tetrachloride; but S. U. Pickering (*Chem. Soc. Trans.*, 1879, 654) subsequently contended that this higher chloride was Mn_2Cl_6 , his arguments being that when manganese dioxide is dissolved in chlorhydric acid and the solution is poured into water, the amount of dioxide in the precipitate is never more than about 47 per cent of the amount originally used. According to this observer, when the dioxide is dissolved in

chlorhydric acid, manganese sesquichloride is formed, two atomic proportions of chlorine being liberated; when, however, the dissolution of the dioxide is performed in the presence of manganous chloride, the amount of dioxide recovered on precipitation by water is largely increased, this increase being in a greater proportion up to the addition of one molecule of MnCl_2 , and, hence, it would seem to show that this chloride combines with the two atoms of chlorine set free on the dissolution of the dioxide in the acid to form another molecule of Mn_2Cl_6 .

In the present paper the author shows that when manganese dioxide is dissolved in chlorhydric acid, even at ordinary temperatures, of the total amount of chlorine which, on Pickering's supposition, should be evolved almost immediately, less than half is evolved, even in the course of five hours; at -18° chlorine is evolved much more slowly, and at -26° C. only 0.35 per cent of the available chlorine was found to be evolved when air was drawn through the solution during two hours. That this could not be due to the formation in the solution of a solid chlorine hydrate would appear to follow from the observation that no such substance was formed when pure chlorhydric acid was saturated with chlorine at -26° C. It must, therefore, be supposed that the original product of the action of chlorhydric acid on manganese dioxide is the tetrachloride, and that no chlorine is at first formed.

In order to ascertain whether, when the tetrachloride of manganese decomposes an intermediate chloride such as Mn_2Cl_6 is formed, weighed quantities of the dioxide were introduced into the bulb of a Victor Meyer's apparatus surrounded by a bath of water at temperatures varying from 38° C. to 63° C., and known volumes of chlorhydric acid were poured in; the volume of air expelled by the chlorine was measured at half-minute intervals. When the results thus obtained were represented in the form of curves, of which the ordinates represented the volumes of gas evolved and the abscissæ the time, it was found that the curves were perfectly regular; this could not be the case if an intermediate chloride such as Mn_2Cl_6 , more stable than the original tetrachloride, were formed in the solution. The curves expressing the rate of evolution of chlorine from solutions of Mn_2O_3 and Mn_3O_4 in chlorhydric acid were also perfectly regular, which shows that in the one case no chloride such as Mn_3Cl_8 intermediate between Mn_2Cl_6 and Mn_3Cl_8 was formed, and in the other case that no chloride such as $\text{Mn}_4\text{Cl}_{10}$, intermediate between Mn_3Cl_8 and MnCl_2 was formed. These curves, therefore, show that on dissolving any of the oxides of manganese: MnO_2 , Mn_2O_3 , and Mn_3O_4 , the only higher chloride formed is MnCl_4 .

It was also found, contrary to Pickering's statement, that the amount of MnO_2 recovered on precipitating the solution was not always under, but always over 50 per cent at ordinary temperatures, the amount recovered being increased by performing the dissolution of the dioxide in chlorhydric acid saturated with chlorine. The fact that the addition of MnCl_2 to the solution increases the amount of MnO_2 recovered is only what we should expect, just as Wurtz found that PCl_5 dissociated to a less extent when vaporised in PCl_3 vapour.

Special Meeting, May 8th.

Fellows who desire to exhibit objects at the Special Meeting in May are requested to communicate *forthwith* with the Secretaries, in order to give time for the preparation of a descriptive list of the exhibits.

An Arrangement of the Stirrer in taking Melting-Points.—E. C. Holtz (*American Chem. Journal*).—The stirrer is fastened in a cork supported by a horizontal stiff spiral wire 25 to 30 c.m. in length; its other end is fixed in a perforated cork which slides on the rod of an ordinary support, and can be placed at any required height.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 14, April 8, 1890.

The Normal Presence in the Chyle of a Ferment which Destroys Sugar.—R. Lépine.—The author has discovered a ferment elaborated by the pancreas which destroys sugar. If the pancreas is absent, or if it is experimentally removed, diabetes ensues.

A Fundamental Property Common to the Two Classes of Spectra. Distinctive Characters of Each Class. Periodic Variations of Three Parameters.—H. Deslandres.—This paper will be inserted in full.

The Suppression of Halos in Photographic Proofs.—Paul Henry and Prosper Henry.—The authors succeed in avoiding these halos by covering the back of the plate with a layer of normal collodion holding in solution a small quantity of chrysoidine. This varnish having an index of refraction little different from that of glass, completely suppresses the halos.

Phosphotrimetungstic Acid and its Salts.—A. Péchard.—This acid is obtained on evaporating to dryness at temperatures below 100° a mixture of phosphoric and metatungstic acids in any proportions. If the phosphoric acid is in excess the mixture, on being taken up in water and submitted to evaporation, yields only the phosphotrimetungstic acid. In the contrary case crystals of this acid are deposited. It appears in the form of non-efflorescent crystals, soluble in water and alcohol. A number of the salts of this acid are described.

A Nitroso-chloroplatinate.—M. Vèzes.—This compound, along with potassium chloroplatinate, is obtained on pouring an excess of hydrochloric acid into a saturated solution of potassium platinonitride. Its composition is given as $\text{PtCl}_3(\text{NO})_2\text{KCl}$.

On Glycolic Nitrile and the Direct Synthesis of Glycolic Acid.—Louis Henry.—Glycolic nitrile is a liquid similar to water, very mobile, colourless, inodorous, and of a peculiar sweetish taste. Its sp. gr. at 12° is 1.100. It congeals at -72° in a mixture of ether and carbonic snow. It is very soluble in water, alcohol, and ether; insoluble in carbon disulphide, chloroform, and benzene. If mixed with rather more than double its weight of fuming hydrochloric acid there is a violent reaction; ammonium chloride is deposited and there is formation of glycolic acid.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6.

Electrodes in Glass Vessels with Mercurial Contacts.—F. Heerwagen (*Instrumentenkunde*).—The arrangement is shown in an accompanying cut.

Apparatus for working with Hydrofluoric Acid.—E. Cohen (*Chem. Centralblatt*).—The author prefers the old method of opening up refractory minerals in a large lead vessel fitted with a cover. Fluor-spar and sulphuric acid are placed in its bottom and the specimens to be acted upon are placed one above each other, stairlike, in small flat leaden dishes. Another apparatus for working with hydrofluoric acid is proposed by H. C. Andersch (*Chemiker Zeitung*), but it requires the accompanying figure.

Automatic Apparatus for Regulating the Time of Boiling.—Felix Bauer (*Chemiker Zeitung*).—For the details the author is referred to the original.

Tubes for Heating Substances under Pressure.—H. N. Warren.—From the *CHEMICAL NEWS*.

A Refrigerator for Use in Distillations.—Carl Schlarb (*Chemiker Zeitung*).—The apparatus is shown in an accompanying figure.

A Spirit Blast-Lamp.—R. Rosenlecher (*Chemiker Zeitung*).—An instrument to be used in place of the gas-blast.

The Meldometer.—J. Joly.—From *Industries and Journ. Soc. Chem. Industry*.

Apparatus for Separating and Shaking Out.—R. Schülze (*Chemiker Zeitung*).—A graduated cylindrical receiver for reading off the volume of a distillate.

Pouring out Acids.—L. M. Denies (*American Chem. Journal*).—To the carboy is attached an instrument similar to the mouthpiece of a washing-bottle, air being supplied with a caoutchouc blast instead of with the mouth.

The Purity of Reagents.—M. von Nencki (*Monatshefte für Chemie*).—Copper oxide and lead chromate used in elementary organic analysis are often impure, the former containing lime and the latter lead oxide. The former is detected by extracting the copper oxide with warm dilute acetic acid, throwing down the copper from the solution by means of sulphuretted hydrogen, and then testing the filtrate with ammonium oxalate. The lead oxide in the lead chromate is detected by extraction with dilute acetic acid and precipitation with sulphuric acid. It amounted in one case to 13.27 per cent. L. L. de Koninck (*Angewandte Chemie*) detected manganese peroxide in lead peroxide. He heats a portion of the sample with an excess of concentrated sulphuric acid until it is completely decomposed, and, when cold, treats with water and a fresh portion of the peroxide. On re-heating the red colour of permanganic acid appears if manganese is present.

Ether.—The so-called pure commercial article always contains various impurities which, on spontaneous evaporation, remain behind as an ill-smelling residue. Sulphur is detected by shaking up the sample in question in a test-tube with a drop of pure bright mercury. If the quantity of sulphur is very small the surface of the mercury is merely rendered dull and grey. If there is much sulphur the entire liquid turns grey or black. Pure chloroform does not reduce alkaline permanganate unless a trace of alcohol is present. Bertram Blount (*Analyst*) describes a series of impurities in so-called pure reagents. P. Lohman (*Pharm. Zeitung und Chemiker Zeitung*) discusses the purity of commercial reagents required in chemico-legal investigations. Zinc and sulphuric acid can easily be obtained free from arsenic. Hydrochloric acid which fulfils the requirements of the *Pharmacopœia* may contain traces of arsenic. Hydrochloric acid freed from arsenic by means of tin is usually stanniferous. Chloric acid may contain arsenic and usually contains baryta.

Preservation of Sulphuretted Hydrogen in Solution.—D. Lindo.—From the *CHEMICAL NEWS*.

Purification of Mercury.—H. Nagaoka (*Tok. Sugaku und Annalen der Physik*).—A modification of Bohn's distillatory apparatus.

Iris-Paper is recommended by W. Greenwalt (*Chemiker Zeitung*) as test-paper for alkalimetry and acidimetry. It is obtained by steeping filter-paper in a watery extract of *Iris versicolor* prepared hot. In a neutral state it is blue, and is turned red by acids and green by alkalis.

Separation of Lime, Baryta, and Strontia.—M. Kupferschläger.—*American Journ. Pharmacy and Chemiker Zeitung*.

Separation and Determination of Zirconia.—G. H. Bailey.—From the *Journal of the Chemical Society*.

Detection of Ferric Salts in Strong Acids.—F. P. Venable.—From the *Journal of Analytical Chemistry*.

MISCELLANEOUS.

Improved Bunsen Burner.—We have received from Messrs. J. J. Griffin and Sons, Garrick St., an improved Bunsen burner which appears to possess many advantages over the old form of burner. The burner consists of three pieces only, easily taken apart and put together. The usual central gas jet is dispensed with, and by one single movement the supply of gas and air are simultaneously regulated. The gas passes into the burner through a way cut in the side of the tube, which is open from top to bottom, and cannot, therefore, become choked.

MEETINGS FOR THE WEEK.

- MONDAY 28th.**—Medical, 8.30.
Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
- TUESDAY, 29th.**—Royal Institution, 3. "The Place of Oxford University in English History," by The Hon. George C. Brodick, D.C.L.
Institute of Civil Engineers, 8.
- WEDNESDAY, 30th.**—Society of Arts, 8. "Photographic Lenses," by T. R. Dallmeyer.
Geological, 8.
- THURSDAY, May 1st.**—Royal Institution, 1.30. Annual Meeting.
Royal Institution, 3. "The Heat of the Moon and Stars" (the Tyndall Lectures), by Prof. C. V. Boys, A.R.S.M., F.R.S.
Society of Arts, 8. "Design Applied to Wood-carving," by Lewis F. Day.
Royal, 4.30.
Royal Society Club, 6.30.
Chemical, 8. "The Conditions under which Hydrogen Peroxide is Formed from Ether," by Prof. Dunstan and T. S. Dymond.
- FRIDAY, 2nd.**—Royal Institution, 9. "Theophile Gautier," by Walter H. Pollock, M.A.
Physical, 5. "Distribution of Flow in a Strained Elastic Solid," by Chas. A. Caras-Wilson. "Photographs of Rapidly Moving Objects," by C. V. Boys. "The Oscillating Electric Spark," by C. V. Boys.
Geologists' Association, 8.
- SATURDAY, 3rd.**—Royal Institution, 3. "Colour and its Chemical Action," by Captain W. de W. Abney, F.R.S.

THE LONDON HOSPITAL MEDICAL COLLEGE.

THE SUMMER SESSION WILL COMMENCE ON THURSDAY, May 1st.

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SCHOLARSHIPS AND PRIZES.—Twenty Scholarships and Prizes are given annually. Students entering in May are eligible to compete for the four Entrance Scholarships in September. Luncheons or dinners, at moderate charges, can be obtained in the Students' Club.

N.B. Special arrangements have been made to meet the requirements of the Examining Board in England so as to enable Students entering in May to pass Part I. (Chemistry and Chemical Physics), and Part II. (Materia Medica and Pharmacy) of the First Examination in July.

The London Hospital is now in direct communication with all parts of the metropolis. The Metropolitan, District, and other railways have stations within a minute's walk of the Hospital and College.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1588.

SOME OBSERVATIONS ON PRECIPITATION.

By GEORGE WATSON, F.C.S.

SEVERAL cases of precipitation are known in which scratches, formed on the sides of the containing vessel, become traced out with a deposit of precipitate while the rest of the glass surface remains otherwise quite uncoated. In some cases—as, for instance, the precipitation of ammonio-magnesian phosphate from weak solution—the scratches appear to exert an attractive force on a liquid in which exists a precipitating tendency or stress, in this way attracting and fixing a precipitate during its formation; in other cases, as I have had occasion to notice, they attract and fix a precipitate after it has been thrown down.

Although this phenomenon has long been known and, indeed, observed by every chemist, I am not aware that anyone has hitherto attempted to explain it, or, in fact, thought that it required any explanation, the remark that the roughened surface of the abrasion acted as nuclei, to which the precipitate attached itself, being considered a sufficient one. This, to my mind, is no explanation, but if, on the contrary, it be viewed as due to the surface-energy of the glass becoming augmented or rendered more potent by abrasion, then, I think, the statement offers a partial explanation of the phenomenon, but not a complete one, for some other factor must be also concerned, otherwise all precipitates, no matter what their nature, would be liable to fixation. This factor I believe to consist in a condensation change in the precipitate from a less to a more dense condition, resulting in the crystalline state, as the two precipitates (basic antimonious chloride and calcic hydric orthophosphate) which I have examined are, when newly thrown down, amorphous and bulky, but pass on standing into heavier crystalline states, and until this change has taken place no precipitate is seen to become fixed on the scratches.

It is not perhaps advisable to take up space with a minute description of the experiments I have made on this subject, a general description, with a summary of the results obtained, being all that is necessary. In the experiments with basic antimonious chloride, a solution of antimonious chloride was made by digesting strong hydric chloride with excess of antimonious oxide in the cold, then filtering and clearing up the somewhat turbid filtrate by the cautious addition of strong hydric chloride. To 100 c.c. of distilled water were then added 5 c.c. of this solution, the whole mixed by agitation, and a number of scratches made on the internal surface of the glass by means of a pointed glass rod. By operating in this way, the following points were noted:—

(a). No fixation occurred until the precipitate had changed into the heavy crystalline condition.

(b). After this change had taken place, new scratches made on the glass were unable to fix any more precipitate on shaking up.

(c). Scratches which had once done work by fixing precipitate, and which had been cleaned from adhering precipitate by washing with hydric chloride and rinsing, were unable to again fix any precipitate when placed in suitable conditions.

(d). Scratches which had already fixed precipitate, but which had only been cleaned by rubbing with a rubber-tipped rod, were apparently sometimes able to again fix a new small quantity of precipitate, this result being probably due to some condensed precipitate from the previous operation still adhering to the glass, as will be shown hereafter.

Similar results are obtained in the case of calcic hydric orthophosphate; my experiments with this substance being made by mixing 50 c.c. of a cold saturated solution of ordinary sodic phosphate with 100 c.c. distilled water and 30 c.c. of a 5 per cent solution of calcic chloride.

But a further study of these experiments leads to other conclusions. Thus, if the adhering precipitate of basic antimonious chloride or of calcic phosphate be rubbed off an abrasion, the latter is found to be a mere hair line in width, while the adhering film of precipitate has a width many times greater. This suggests the idea that the film has grown in width by a process analogous to the growth of a crystal, for, if we imagine the path of the abrasion to be first filled up with a line of condensed precipitate, the widening of this line could only occur by the condensed precipitate itself exerting an attractive force on the contiguous uncondensed precipitate. This, evidently, amounts to saying that the rate of condensation in the case of these precipitates is an accelerating one. Hence, if a quantity of either precipitate be formed in admixture with a preformed quantity of the condensed variety, the periods of time now required for their mutual condensations should be less than those required if no preformed condensed precipitate were present. This I find to be the case; for example, 5 c.c. of the antimonious chloride solution used in the former experiments were precipitated with 100 c.c. of water as usual, allowed to condense, and the clear supernatant poured off. Another 100 c.c. of water were then poured on, another 5 c.c. of antimony solution added, and the whole shaken up. At the same time, a parallel experiment was started, but without having any condensed precipitate previously present, and both glasses were shaken up simultaneously three times at intervals of five minutes. At the end of this time the parallel experiment was unchanged, while in the other the precipitate was completely condensed into the heavy crystalline state. This experiment becomes very striking when performed on a large scale—say, with 50 gallons of water and antimony solution in proportion.

Similar results are obtained in the case of calcic hydric orthophosphate. Thus, 50 c.c. of water, 15 c.c. of a 5 per cent solution of calcic chloride, and 25 c.c. of a cold saturated solution of disodic phosphate were mixed in a test-glass and allowed to condense. The supernatant was poured off the precipitate, and 50 c.c. of water added, then 15 c.c. of the calcic chloride solution, and 25 c.c. of the sodic phosphate solution. A parallel experiment was done at the same time, in every way comparable with the exception of lacking the preformed condensed precipitate. Both glasses were shaken up simultaneously and allowed to stand at rest. Within ten minutes the precipitate, which had been formed in contact with the condensed variety, had settled, leaving a perfectly clear supernatant, while the other had not settled in the least.

These results suggest an analogy to the sudden crystallisation of supersaturated solutions produced by dropping into them a crystal of the dissolved salt. Just as these precipitates rapidly pass from a more to a less tenuous condition on admixture with a quantity of the condensed variety, so in such solutions the dissolved salt rapidly passes from the tenuous state of solution to the condensed state of the crystal on the introduction of a small quantity of the latter. Whence, by analogy, it follows that these cases of crystallisation are condensation changes proceeding at accelerating rates, and it is because they are such that the introduction of a minute crystal of the dissolved salt can bring about the rapid crystallisation of the whole. If they were not such, the crystallisation could not be induced by these means.

As there are some cases—as, for instance, the precipitation of ammonio-magnesian phosphate from weak solution—in which also the precipitate shows this property of fixing itself to abrasions, it may be assumed that similar causes are concerned here, viz., the potent surface-energy of abraded glass combined with the simultaneous occurrence of a condensation change. Whence, going by

analogy, precipitation also, considered generally, comes to be viewed as a condensation change proceeding at an accelerating rate. What appears in most cases as an instantaneous change is, in reality, an accelerating change with an enormously large increment of acceleration. It also follows from analogy that the presence of preformed precipitate in the liquid should not only hasten the starting of precipitation in those cases in which precipitation would start of itself, but should also cause precipitation in those cases in which no precipitate would form of itself. This latter deduction is illustrated in the experiments of Baubigny on the precipitation of nickelous sulphide (CHEM. NEWS, vol. xlv., p. 257, 1882), while the former is exemplified by an observation which I have made during the precipitation of arsenic as sulphide when freeing quantities of phosphoric acid from that impurity. Working with a quantity of 9 or 10 gallons of liquid containing about 50 per cent of H_3PO_4 after the precipitation is fairly under way, but still incomplete, if the current of hydric sulphide be stopped and the precipitate allowed to settle, the supernatant is seen to have a yellowish opalescent appearance. On stirring up vigorously, the precipitate already formed seizes, as it were, the incipient precipitate and pulls it out of solution, leaving, on settling, a clear, or nearly clear, supernatant. The precipitate, at this point, is in the form of large semi-curdly flakes, but after a while these change into smaller and heavier ones, which can again go through the same operation on further gassing with hydric sulphide.

Since writing the above, I have reason to believe, from a further experience of this method of freeing phosphoric acid from arsenic, that the appearances described above only happen when the precipitation is started in the heat, and when a somewhat large proportion of arsenic is present. If the amount of arsenic present be small, and the precipitation wholly conducted in the cold, the sulphide of arsenic is thrown down in a finely-divided state, and only settles after standing for several days.

NOTE ON THE ADMIXTURE OF ETHYLIC ALCOHOL WITH WATER.

By THOMAS FARRINGTON, M.A., F.C.S., F.I.C.

It is well known that a slight rise of temperature takes place when alcohol is mixed with water. This phenomenon has seemed to me worthy of quantitative examination, with the view of ascertaining the exact proportions of the liquids which produce the greatest heat effect, and what that heat effect amounts to.

From numerous preliminary experiments I have ascertained that the greatest rise of temperature is about $10^{\circ}C.$, and occurs with mixtures containing from 28 to 50 per cent of alcohol by volume, there being comparatively little variation of final temperature between these limits.

Assuming that the specific heat of mixtures of alcohol and water is directly proportional to the volumes of the components, the greatest heat-effect would occur with a mixture containing 33 per cent of alcohol. As this proportion does not coincide with that which gives rise to the greatest contraction in volume, I intend to further investigate the question with a view to ascertaining if the

two phenomena coincide when the following difficulties in the way of accurate results are overcome:—

1. The specific heat of the resulting compound may not be the same as that calculated in the above manner from those of its components.
2. The evolution of dissolved gases which results on mixing must render the temperature observation incorrect; the liquids must consequently be made and kept apneumatic before mixing.
3. The rise of temperature may interfere with the formation of the probable compound; and in such a case it must be arranged to have the final temperature the same in comparative trials of different mixtures, or the heat must be measured without any final elevation of temperature by the use of the ice calorimeter or such other means.

Through the kindness of Prof. Hartog, of the Queen's College, Cork, I have been able to measure the refractive indices of some mixtures of water and alcohol, and find that the results agree with those calculated from the ordinary formula. As the densities of the solutions are important factors in this formula, it seems certain that the variations in the refractive index follow those in the density. The table below gives (1) the volumes of the components; (2) the specific gravities; (3) the refractive indices, (a) observed, (b) calculated from the formula, (c) calculated from the volumes of the components; (4) the difference of the observed and "mean" refractive indices.

From this it appears that the abnormal variation in the refractive index is greater at the point where the greater contraction in volume occurs.

The most remarkable difference in physical properties between mixtures of alcohol and water and the liquids themselves is that which manifests itself when they run through a comparatively small opening; this phenomenon was observed in the following manner:—The glass stop-cock of a burette was so set that the contained liquid might drop slowly out, and the time that equal volumes of the three liquids took to run out was noted. The average of three fairly concordant experiments in each case gave, for the time of running out from the zero point to the end, the following times:—

Water		240 seconds.
Alcohol		270 "
Mixture	{ Alc. = 1 H ₂ O = 2 }	.. 346 "

Fearing lest chance filaments might possibly have influenced this result while the liquids ran through so small an aperture, I have confirmed the foregoing experiments by others in which they were allowed to run through the fully opened stopcock. Each result is the average of seven close determinations, the times being taken with the help of a stop-watch.

Water		20.9 seconds.
Alcohol		22.7 "
Mixture		26.9 "

It thus appears that the complex and loosely-combined molecules of ethyl alcohol hydrate find much more difficulty in passing through a small aperture than the smaller molecules of alcohol and water.

4, Waterloo Place, Cork,
April 19, 1890.

	(1) Volume of		(2) Specific Gravity.	(3) Refractive Index.			Difference of (a) and (c).
	Alcohol.	Water.		(a) Observed.	(b) Calculated.	(c) Mean.	
Alcohol	—	—	0.7978	1.3645	—	—	—
Water	—	—	0.9990	1.3320	—	—	—
Mixture	5	10	0.9610	1.352	1.3535	1.343	0.009
Mixture	5	5	0.9348	1.361	1.3622	1.348	0.013

METEORIC ORIGIN OF THE DIAMOND.

HERR A. MEYDENBAUER, writing in the *Bayr. Industr. und Gewerblatt* (thence copied into the *Chemisch-techn. Central Anzeiger*), states that as far back as 1874 he wrote in "Sirius" that "The diamond can only be of cosmic origin, having first arisen simultaneously with the primitive rocks, and having also fallen as a meteorite at later periods of the earth's formation. An appropriate examination of the places where it occurs would elucidate this dark point."

Such an investigation was not undertaken for some time. Dr. Kersten produced, in 1887, an essay on the peculiar features of the occurrence of the diamond. The English geologist, B. H. Carwill, without having the meteoric origin of the diamond in view, remarked that the matrix of diamonds in South Africa had a remarkable similarity to certain meteorites with which he was well acquainted. Finally, two Russian *savants*, on examining a black meteorite which fell on September 4, 1886, at Nowy Uray, in the Government of Pensa (a portion of which is in the Natural History Museum of Vienna), found diamonds in small crystals amounting to one per cent of the total stone.

Whilst all minerals of which the earth is composed, whether primitive, stratified, or metamorphic, possess the same attributes in all latitudes, the diamond occurs in practically available specimens only in a zone of the southern hemisphere extending through Southern Asia, South Africa, and South America. Its alleged occurrence in very small and worthless crystals in the Itacolumite of the Ural does not contradict this derivation, since, according to the author's view, the massive primitive rocks have a similar though more ancient origin.

The above available localities of the diamond contain the residues of not very compact meteoric masses which may, perhaps, have fallen in historical ages, and which have penetrated more or less deeply, according to the more or less resistant character of the surface where they fell. Their remains are crumbling away on exposure to air and sun, and the rain has long ago washed away all prominent masses.

The enclosed diamonds have remained scattered in the river beds, whilst the fine light matrix has been swept away. At the spots where the meteorites fell, and which, from their superficial appearance, did not in the least indicate what was within, there was, above all things, no indication of volcanic action. The information received about the structure of the pits in South Africa agrees completely with the phenomena attending the fall of masses from above, whilst the superficial appearances which attend volcanic action are quite wanting. The matrix contains all the ingredients necessary for a readily fusible slag, and yet there is no trace of fusion, a fact generally overlooked. As to the diamond, which cannot support even a red heat, the hypothesis of a subsequent action has been invented, though there is nothing analogous either in nature or in the artificial circumstances of our laboratories. On the other hand, the traces of heat on the margins and the erect stratification of the adjacent rocks are sure signs of matter striking in from above.

Very decisive is the absence of depth in the adjacent rocks. Never has there been found a cavity or a crevice going down to unknown depths, without which a rise from the earth's interior is unthinkable, and in which, on the supposition that diamonds come from below, they would be found in masses. On the contrary, we hear of exhausted pits, especially in Brazil. The diamond-bearing meteors were there either masses of little density, or they struck upon very hard rocks, burst in all directions, and scattered their rich contents all round. The diamonds found their way into the beds of streams, which became the diggings of the future. That pockets may still remain in clefts and ravines is very probable.

In India the process has undergone modifications

which testify to the accuracy of our supposition. Whilst Cape diamonds are found in the matrix with a surface clear as glass, the Indian diamonds are covered with a blackish crust, as if singed superficially. As constituents of small but numerous meteors of an otherwise pulverulent mass, they were, whilst passing through the atmosphere, exposed for a moment to the action of heat.

The pulverulent mass was retained in the air as the well-known train of the larger meteors, and the diamonds fell to the ground as true meteorites. The diamond is, therefore, a gift of Heaven!

RELATIONS BETWEEN THE COMPOSITION AND THE ABSORPTION-SPECTRA OF ORGANIC COMPOUNDS.

By M. ALTHAUSSE and G. KRÜSS.

G. Krüss has already found in a great number of organic compounds that the introduction of methyl, oxy-methyl, and carboxyl groups, i.e., those which increase the proportion of carbon in a compound, displace all the absorption bands of a spectrum towards the red. He finds, further, that the bands are displaced towards the blue end of the spectrum if an atom of hydrogen in an organic compound is replaced by a nitro- or amido-group. The authors have verified these conclusions by further experiments, and show that an addition of hydrogen to an organic colouring-matter displaces its absorption towards the blue. If a careful spectroscopic determination is made, what kinds of light are transmitted by the technical solution of a colouring-matter, and which are lost, it can be predicted with moderate accuracy what will be the colour of a substitution derivative of the original colour. If this colour displays in the spectrum a band which absorbs the blue, then on introducing ethyl or methyl a substance is obtained which has in its colour more blue and less green. If the original substance has an absorption band in the red its colour will become redder by ethylation, the band being displaced towards ultra red.—*Deutsche Chem. Gesellschaft Berichte*.

THE SEPARATION AND DETERMINATION OF TIN AND TITANIUM, WITH ESPECIAL REFERENCE TO THE ANALYSIS OF SILICATES

By A. HILGAR and H. HAAS.

THE simultaneous occurrence of stannic and titanic acids in silicates occasions much trouble. The most suitable method for their separation is founded on the fact that mixtures of stannic and titanic acids are reduced in a current of hydrogen at dull redness in such a manner that the stannic acid becomes metal, but titanic acid not. From this mixture, the reduced metal can easily be dissolved out by hydrochloric acid, at 20 per cent, without titanium being dissolved.

The mixture of stannic and titanic acids is placed in a tube of sparingly fusible glass, 15 to 20 c.m. in length, and ignited at dull redness for a quarter of an hour in a current of hydrogen by means of a small Bunsen burner, and then let cool in the current. The reduced mass then rinsed into a beaker with a little water and a few drops of hydrochloric acid, if needed, covered with 30 c.c. of hydrochloric acid at 20 per cent, kept at a gentle boil for half an hour, replacing the liquid as it evaporates, and filtered when cold. From the faintly acid filtrate the tin is precipitated by means of sulphuretted hydrogen, the tin sulphide is washed with water containing ammonium acetate, again reduced in a current of hydrogen, and the

reduced tin is finally converted into stannic acid by means of nitric acid, and weighed as stannic oxide.

The contents of the filter obtained after treatment with hydrochloric acid containing titanium are burnt along with the filter, ignited, and fused in a platinum crucible along with 10 parts of potassium carbonate. The melt is soaked in about 200 c.c. of water, concentrated sulphuric acid is added drop by drop until the acid titanate is dissolved, neutralised with solid sodium carbonate, 2 grms. of concentrated sulphuric acid are further added, the liquid is made up to 400 c.c. and kept at a boil for six hours. All the titanic acid is separated out, and, after filtration and ignition, it is washed as titanium dioxide.

The analysis of stanniferous and titaniferous silicates is conducted as follows:—5 to 10 grms. of the sifted minerals are stirred up to a thick paste with water in a platinum capsule, mixed with dilute sulphuric acid (1 : 10) till the mixture becomes thin, fuming hydrofluoric acid is gradually added until the silica is completely removed, high temperatures being especially avoided. When the decomposition of the mineral is complete, and the hydrofluoric acid driven off, the mass is brought to a pasty consistency on the water-bath, rinsed with water into a beaker or a porcelain pan, neutralised with potassium or sodium hydroxide, mixed with two grms. strong sulphuric acid, made up with water to 400 c.c., and kept for six hours at an unbroken boil. The quantities of stannic and titanic acids are thus completely separated in a hydrated state. In the precipitate, which may, at the utmost, contain a little iron, the separation of tin and titanium is effected as already described. The filtrate from this precipitate serves for the determination of the other ingredients of the silicate.—*Berichte d. Deutsch. Chem. Gesellschaft*, vol. xxiii., p. 458.

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Continued from p. 185).

In this qualitative detection of mercury which is always successful, even with very small quantities of mercury, a too prolonged digestion of the brass wool in the liquid must be avoided, since then, in spite of treatment with purifying agents, the organic matter remains deposited upon the brass-wool, when the formation of empyreumatic products interferes with the detection of mercury. In all cases the author therefore places in front a short stratum of copper.

When mercury is present in larger quantities it can be recognised with the naked eye on the amalgamated brass threads. The further chemical detection may be executed in a test-tube in the known manner.

The quantitative determination of mercury is conducted as follows:—Sulphuretted hydrogen is passed into the hot hydrochloric liquid, the precipitate is filtered through a plug of asbestos (previously ignited and well purified with *aqua regia*) in a filter of medium size, and washed with hot strong hydrochloric acid until it runs off colourless. If arsenic sulphide is present the precipitate must undergo a preliminary digestion with yellow ammonium sulphide. The funnel is then inverted, and the asbestos plug, along with the mercury sulphide, is washed with the same acid into a beaker, the funnel is rinsed, and, with the addition of a few drops of nitric acid, cautiously heated until all the mercury sulphide is decomposed, and single flakes of sulphur float about in the liquid. The nitric acid is only to be added in the quantity just necessary, since the mercury sulphide dissolves readily on its addition even in small quantities. The expulsion of the excess of nitric acid is not necessary and not practicable, but any excess may be neutralised. The asbestos is then collected together into a lump by

means of a glass rod, re-introduced into a funnel, and the liquid, which is turbid from asbestos fibres, and from mercury which has escaped oxidation, is again filtered through the plug. If it drops through turbid, it is returned to the funnel until it runs clear. The asbestos is then well washed, the filtrate, which contains hydrochloric acid and a little nitric acid, is diluted with water and mixed with an excess of phosphorous acid. After twenty-four hours, the pure white mercurous chloride is filtered off, washed successively with water, alcohol, and ether, and weighed upon a filter. In the determination of mercury chloride two sources of loss must be remembered: its possible reduction on contact with organic matter, which should hence be avoided, and, secondly, its ready volatility, whence strong heat and great concentration of the liquids should not be applied.

β. Detection and Determination of Antimony.

Fifty c.c. of the liquid are placed in a bright platinum capsule, the excess of acid is partially neutralised with ammonia, and a piece of zinc is introduced. After six hours the liquid is decanted off and the capsule rinsed out with a little water. The smallest quantities of antimony may be recognised by brownish black spots which appear at the bottom and the margin of the platinum dish. A longer action of the zinc should be avoided, as antimony is soluble in concentrated solutions of zinc chloride. It must be remembered that in alloys of antimony and tin the former metal is not indicated by this test if its proportion is 5 per cent, and very doubtfully if it reaches 10 or even 20 per cent. It is therefore necessary in such cases to remove the bulk of the tin by fusion with caustic soda, and applying the above test to the portion insoluble in water.

The author has been compelled to abandon the detection of antimony by means of its volatile hydrogen compounds.

For the determination of antimony, sulphuretted hydrogen is passed into the slightly acid solution, at first at a boiling heat and then, after the removal of the flame, until it is cold. After the precipitate has fully settled, at the expiration of the third day, the excess of sulphuretted hydrogen is expelled by the introduction of a strong current of carbonic acid. If frothing sets in it may be prevented by the addition of ether. The precipitate is filtered off, washed with ammonium acetate, rinsed from the filter into a flask by means of hot dilute solution of sodium sulphide, and into the hot solution sulphuretted hydrogen is passed until it smells strongly of the gas. The contents are filtered, the precipitate washed with dilute sodium sulphide containing sulphuretted hydrogen, the washings are added to the filtrate, which is then, whilst being stirred, mixed very carefully with hydrochloric acid in slight excess. After the first violent reaction is over, the whole is gradually heated and raised to a boil. After twenty-four hours the precipitate is filtered off, washed with ammonium acetate, rinsed into a porcelain capsule, the filter washed with hot solution of sodium sulphide, the contents of the capsule are evaporated upon the water-bath, and cautiously treated at repeated intervals with nitric acid until no further reaction takes place. The residue is moistened with soda-lye, intimately mixed with dry sodium carbonate, the mixture dried and gradually introduced in small portions into melted sodium nitrate in a silver crucible, which consumes the organic matter present. The melt, when cold, is at once lixiviated with water in the silver crucible, the solution is poured into a beaker and allowed to settle.

In twenty-four hours the precipitate, which has a blackish colour from the presence of a little silver or silver oxide, is filtered off and washed with alcohol at 45 per cent containing soda. After a caoutchouc tube has been drawn tightly over the neck of the funnel and tied firmly, it is closed with a clip, and the precipitate is lixiviated for half an hour with a hot solution of tartaric and hydrochloric acids. The clip is then opened, and the liquid is

let off into a beaker. If not clear, it is repeatedly returned to the filter until a clear filtrate is obtained. The residue is washed with a dilute hydrochloric-tartaric solution until the filtrate, even on prolonged standing, no longer gives a reddish precipitate with sulphuretted hydrogen. The washings are then added to the filtrate, concentrated on the water-bath, the excess of acid is neutralised with ammonia, and sulphuretted hydrogen is again introduced into the solution. The antimony sulphide precipitate must have a pure orange colour. Its conversion into antimony antimoniate requires much care and patience, and all the precautions laid down by Bunsen must be closely adhered to. In place of the porcelain cover, convex internally, the author uses a watch-glass during the oxidation with nitric acid, as in this manner the action of the acid can be better observed and regulated.

The purity of the ignited and weighed residue may be thus ascertained:—The crucible, without a lid, is placed in the reductive space of a large burner. On the internal sides of the crucible there soon appears a blackish grey shining layer of metallic antimony, and in a short time the entire contents of the crucible have disappeared if consisting of pure antimony antimoniate. Of course, the antimony cannot then be reserved as an exhibit. In many cases, where the quantity of tin oxide present is not too great, the best result is obtained by determining the antimony from the difference of two weighings.

(To be continued).

ASH DETERMINATION IN RAW SUGARS.*

By F. G. WIECHMANN, Ph.D.

THE method formerly used for determining the ash in sugar consisted in carbonising the sample at a low heat, extracting the soluble salts from the carbonaceous mass by boiling water, igniting the residue, adding this ash to the aqueous extract obtained, and evaporating completely to dryness.

In 1864, Scheibler† published his method of incinerating sugars with sulphuric acid, which proved to possess great advantages over the former method in ease and dispatch of execution. It was only given to the world after the originator had tested it for five years, and carried out by it more than two thousand determinations.

Of course, neither Scheibler's method nor the method of incineration referred to pretend to give the actual amount of salts in the sugar, for by the former the salts are changed into sulphates, while combustion transforms them into carbonates or oxides. Landolt,‡ for instance, holds that the weight of the salts in beet-sugars is about twice the weight of the ash found by analysis.

As the molecular weight of the sulphates is greater than that of the carbonates, Scheibler subtracts 10 per cent from the weight of the sulphate ash, and states that the result is then identical with, or at least corresponds very closely to, the values obtained by the other method. In his paper previously referred to, several analyses are cited in support of this claim.

A cursory search through the literature at hand shows that the method of incinerating with sulphuric acid has been examined into by several chemists, of whom some do not share Scheibler's estimate of its value.

Boivin and Loiseau§ endorsed the method as capable of giving constant results if the combustion were slowly conducted, but claimed that it yielded exceedingly variable values if this condition were not fulfilled. As their experiments, however, were partly carried out under con-

ditions entirely different from those prescribed by Scheibler, their verdict is of little importance.

Dubrunfaut* studied the method chiefly as to the value of the factor 0.9 used in transforming the sulphates into carbonates, and expresses himself as follows:—"In this method sulphuric acid is substituted for the chlorine of the chlorides and for the carbonic acid which is yielded by the organic acid salts and the nitrates. As the relations between the organic acid salts, the nitrates, and the chlorides are very variable in beets, in the molasses, and in the sugars, it stands to reason that the factor 0.9 is nothing but a general average factor which, in many cases, may be considerably far from the truth."

Violette, in an article published in 1873,† states that "this method of incinerating sugars with sulphuric acid, generally adopted at the present time, gives the weight of the ash higher than the true weight of the ash in raw sugars, and this difference is the greater the richer the ash is in salts of soda and alkaline carbonates."

The following year this author wrote a paper entitled‡ "Determination of the Relation between the Real Ash and the Sulphated Ash in the Products of the Sugar Industry," in which he published a table giving a résumé of his researches. This table embraces the analysis of raw sugars, beets, and molasses, and shows the difference between the amounts of the real ash and the values obtained by the sulphuric acid method. The differences exhibited are very considerable in many cases.

H. Leplay, in his "Chimie Théorique et Pratique des Industries du Sucre," p. 207, commenting on these figures and on the conclusions which Violette bases on them, says:—"The most striking conclusion to be drawn from the analyses of M. Violette is that this factor is very variable and does not offer sufficient guarantee of correctness for the transformation by calculation of the weight of the sulphates found by analysis into carbonates."

On the other hand, Von Lippmann,§ after giving the analysis of a carbonate ash of a representative sample of beet-sugar, which will be referred to later on, says:—"It seemed of interest to ascertain the relation of this carbonate ash to the sulphate ash which might be obtained from it. Ten grms. of ash were calcined with sulphuric acid in a platinum muffle, and 11.2008 grms. sulphate ash were obtained. If one-tenth be deducted from this figure, as is done in commercial practice, 10.0807 grms. results, instead of 10 grms., thus demonstrating most perfectly the correctness of Scheibler's factor, 0.9, for this case."

Although primarily applied to the determination of ash in beet-sugars and beet-root products, Scheibler's method won its way into general favour, and soon came to be almost the only method employed in practice, and to be applied indiscriminately to the ash determination of all sugars.

In the course of some research work recently carried out by the author, quantitative determinations were made of the ashes of sugars from various countries.

The scheme of analysis adopted was the following:—

Ten grms. of sugar were dissolved in hot water and filtered;|| the residue was thoroughly washed with boiling water, and the filtrate and washings evaporated to dryness. The mass was carefully carbonised, and then extracted with boiling water until nitrate of silver no longer gave the reaction for chlorine. Solution 1 was evaporated to small bulk. Residue 1 was dried, ignited, and weighed. This weight was noted as insoluble ash. The solution and the ash obtained were combined, hydrochloric acid was added, and the solution evaporated to dryness. All the chlorine was then driven off, the residue taken up

* Journal des Fabricants de Sucre, 18 Decembre, 1870.

† Annales de Chimie et de Physique, 4th Series, vol. xxix., p. 514.

‡ Journal des Fabricants de Sucre, Octobre 22, 1874.

§ Zeitschrift des Vereines für Rubenzucker-Industrie, vol. xxi., 1881, p. 399.

|| This was done in every case to have all the analyses made under the same conditions; in most instances it was imperative, for the inorganic suspended impurities (sand, clay, &c.) in a sample often weighed more than the total sugar-ash.

* From the School of Mines Quarterly, Vol. xi., No. 1.

† Zeitschrift des Vereines für Rubenzucker-Industrie, vol. xiv., p. 188.

‡ Ibid., vol. xviii., p. 68.

§ Journal des Fabricants de Sucre, 6 Février, 1868.

with water and a little hydrochloric acid, and filtered. The insoluble residue in the filter was thoroughly washed, and the washings added to the filtrate. Residue 2 is silica. To filtrate 2 added ammonia hydrate, boiled, and filtered. The Residue 3, iron and alumina, was thoroughly washed, and the washings added to filtrate. To filtrate 3 added ammonium oxalate and evaporated to dryness. The ammonia was burned off, and the oxalates changed to carbonates by adding a little ammonium carbonate, and then again driving off the ammonia. The mass was then taken up with water, filtered, washed, and the washings added to the filtrate. This residue, Residue 4, consists of carbonates of calcium and magnesium. The filtrate was evaporated to small bulk, and moistened with ammonium carbonate.

The evaporation was then continued to dryness, the ammonia cautiously driven off, and the residue weighed. This gave the alkalis in the form of carbonates, and this weight, added to the insoluble ash previously determined, represents the total carbonate ash.

This method, while yielding carbonate ash, avoids the possible loss of alkalis by volatilisation, and practically corresponds to the method in vogue before the introduction of Scheibler's process.

As the data thus obtained were carbonate ash determinations of sugars entirely different in their composition from beet-sugars, and of a description that, at least to the writer's knowledge, has not been much studied, it was decided to make on them ash determinations according to Scheibler's method in order to learn whether the results yielded by the two methods would correspond.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 17th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MESSRS. Fred. A. Anderson, Henry H. Bunting, P. A. Cobbold, and D. S. MacNair were formally admitted Fellows of the society.

Certificates were read for the first time in favour of Messrs. James Kear Colwell, 2, Lloyd Street, Lloyd Square, W.C.; William Tait, 115, Rylston Road, Fulham, S.W.

The following were elected Fellows of the Society:—Joseph Barker, Charles Ridgeway Beck David Corrie, William Dixon, Thomas Flower Ellis, Frederick John Hambly, Andrew Cowan Holburn, B.Sc., C.E., William Frederick Laycock, Ph.D., Arthur Sheridan Lea, Herman Lescher, John Stewart MacArthur, Henry D. Mosenthal, George Müller, Ph.B., E. H. Neville, M.A. Camb., Harold Picton, Ernest George Scott, James Sibun, Alexander Smith, Willis Brewin Shuttlewood, Frederick Richard M. Stone, James S. H. Walker.

The following papers were read:—

28. "Phosphorous Oxide." Part I. By T. E. THORPE, F.R.S., and A. E. TUTTON.

The authors describe a method of making phosphorous oxide in quantity by burning phosphorus in air. Pure phosphorous oxide melts at 22.5°, and solidifies at 21°. It boils unchanged in an atmosphere of nitrogen or carbon dioxide at 173°. Vapour density determinations made by Hofmann's method show that its molecular weight corresponds to the formula P_4O_6 . In this respect it is analogous to arsenious and antimonious oxides, which are respectively represented by the formulæ As_4O_6 and Sb_4O_6 . A determination of the molecular weight by Raoult's method, using benzene, which has no chemical

action on the substance, as a solvent, also indicated the formula P_4O_6 .

On heating phosphorous oxide to about 300°, it is decomposed, and at 440° it is wholly changed into phosphorus and phosphorus tetroxide, $2P_4O_6 = 3P_2O_4 + 2P$. Phosphorous oxide is readily acted on by light, and in bright sunshine its colour rapidly becomes yellow, and eventually dark red. Observations by Captain Abney show that the violet rays are most active in effecting the change. Curves showing the results of the photometric observations are given in the paper.

As first prepared, phosphorous oxide is obtained in minute crystals, aggregated into a snow-like mass. On allowing the melted oxide to cool, it solidifies in the form of thin prisms capped by pyramids; the crystals frequently attain the length of an inch or more.

The crystals appear to belong to the monoclinic system, and exhibit the pinacoidal faces—

$$a = \{100\} \infty P\infty \text{ and } b = \{010\} \infty P\infty,$$

several prism faces, a pair of orthodomes, and a pair of complementary pyramidal faces. The extinctions upon a are parallel to the prism edges, whilst those upon b make an angle of about 20° with the prism edges. When the crossed Nicols are parallel to the orthopinacoidal edges, the brush passes across the centre of the field in a line parallel to the vertical axis. The optic axial plane, therefore, appears to be the symmetry plane b . The crystallographical relations of P_4O_6 , As_4O_6 , and Sb_4O_6 are discussed in the paper.

The relative density of liquid phosphorous oxide was found to be 1.9358 at $\frac{24.8}{4}$. Its thermal expansion, as determined by dilatometrical measurements, is expressed by the formula—

$$V = 1 + 0.0091377t - 0.0011175t^2 + 0.00038607t^3.$$

Its relative density at the boiling-point is found to be 1.6859, whence its specific volume is 130.5. The bearing of this observation on the question of the constitution of phosphorous oxide, and on the question of the varying specific volume of combined phosphorus, is then discussed. Previous observations by one of the authors had shown that the specific volume of combined phosphorus is about 25. From the observations of Pisati and De Franchis, and of Ramsay and Masson, the specific volume of free phosphorus is found to be about 20.9. If all the oxygen in phosphorous oxide be considered as single linked, or, in other words, to have the specific volume 7.8, the specific volume of the phosphorus in phosphorous oxide is 20.9, agreeing with the observations of Ramsay and Masson.

The conclusion to which the authors come is that, whilst the variation in the specific volume of phosphorus may be related to the atomic arrangement of the phosphorus atoms in the molecule of the element, and in that of the phosphorous oxide, both of which contain the same number of phosphorus atoms, this variation is not necessarily dependent on or related to the differences in the combining power of the element.

Determinations of the refractive index of phosphorous oxide for the red lithium line, the sodium D line, the green thallium line, and the three brightest hydrogen lines corresponding to C, F, and G have led to the following general expression for the refraction of liquid phosphorous oxide at 27.4°:—

$$\mu = 1.5171 + \frac{817,670}{\lambda^2} - \frac{316,590,000,000}{\lambda^4}.$$

The calculated value of μ for the line A (wave-length 7604) is 1.5311: for a ray of infinite wave-length it is the first term of the above expression, viz., 1.5171. As the rel. den. of liquid phosphorous oxide at 27.4° is 1.9300, the refraction equivalent of phosphorous oxide for a is—

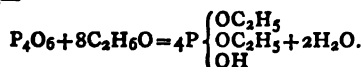
$$\frac{220 \times 0.5311}{1.93} = 60.5$$

for a ray of infinite wave-length it is 58.9.

The bearing of this observation on the refraction equivalent of phosphorus is then discussed.

Contrary to the usual statement of the text-books, cold water has very little action on phosphorous oxide: many days elapse before even a small quantity is dissolved; it then forms phosphorous acid, H_3PO_3 . Hot water acts upon P_4O_6 with explosive violence, forming the red suboxide, phosphoric acid and spontaneously inflammable phosphoretted hydrogen.

Caustic alkalies act similarly. On adding ethyl alcohol to the oxide it at once ignites, but with care the two compounds may be caused to interact to form *diethyl phosphite* or *diethyl phosphorous acid* in accordance with the equation—



This substance, which will be described more fully in a subsequent paper by one of the authors and Mr. Parker North, is a liquid of intensely disagreeable smell, of rel.

den. 1.0749 at $\frac{15.5}{4}$, and boiling at $184-185^\circ$. Ether, carbon bisulphide, and benzene dissolve phosphorous oxide unchanged.

Phosphorous oxide spontaneously oxidises to phosphorus pentoxide on exposure to air or to oxygen, and the process of oxidation is attended under diminished pressure by a faint luminous glow. No ozone is formed as the oxidation proceeds. On gently warming the oxide in oxygen, the glow gradually increases in intensity until it passes into flame. In warm oxygen the melted oxide at once ignites and burns with great brilliancy. Care, therefore, is necessary in distilling large quantities of phosphorous oxide to avoid the free access of air; otherwise dangerous explosions may occur.

In contact with ozone, phosphorous oxide glows at the ordinary temperature and pressure.

A small quantity of the oxide thrown into a jar of chlorine at once inflames, but on leading a slow current of the gas over the cooled oxide it is gradually converted into phosphorus oxychloride and the metaphosphoryl chloride of Gustavson: $P_4O_6 + 4Cl_2 = 2POCl_3 + 2PO_2Cl$.

Phosphorous oxide has a well-marked physiological effect, and it is not improbable that the action hitherto attributed to phosphorus, especially as regards its influence on the glycogenic functions of the liver and on tissue change, may be really due to this substance. It is well known that persons employed in the manufacture of lucifer-matches are occasionally attacked by caries of the lower jaw; this is not due to the action of the phosphorus after absorption into the circulation, but to the direct effect of the fumes upon the bone itself: for it has been found that when a bone of an animal fed by phosphorus was exposed no carious change took place; but if one were exposed to the fumes caries was produced, and amongst lucifer-match makers it has been noticed that only those who have carious teeth suffer from necrosis of the jaw (T. Lauder Brunton, "Pharmacology, &c.," 771). The fumes from phosphorus consist largely of phosphorous oxide; by drawing air over phosphorus without allowing it to ignite, and passing the fumes through a narrow strongly cooled tube, a deposit is obtained which melts with the warmth of the hand and gives the reactions for phosphorous oxide. Moreover, the smell of the product is identical with that of pure phosphorous oxide, and it is also identical with the peculiar smell noticed in a lucifer-match manufactory during the making and handling of the "composition" with which the splints are "tipped," and which hangs about the benches where the "boxers" are at work. It is highly probable, as Schönbein long ago surmised, that phosphorus vapour as such is odourless, and that the smell which phosphorus ordinarily possesses is a mixture of that of ozone and of phosphorous oxide.

The authors are continuing the study of this compound, and have already investigated the action upon it of

ammonia, sulphur, sulphuric acid, the chlorides of phosphorus, &c., and they are also engaged in experiments on its behaviour with a number of organic substances, and they promise a further communication on an early date.

29. "The Action of Chlorine on Water in the Light, and the Action of Light on certain Chlorine Acids." By Professor A. PEDLER.

After referring to the somewhat discrepant statements on record regarding the action of chlorine on water in the light, the author describes a long series of experiments made in Calcutta, where the intensity of light is such that a strong solution of chlorine in water, when exposed to the full blaze of the sun during the hot season, is actually seen to effervesce very decidedly. The results show that interaction takes place only under certain conditions, and that more than one change is possible.

In a first series of experiments, known volumes of chlorine and water enclosed in tubes were exposed to light, and at the conclusion of the exposure the tubes were opened under water: the contraction having been measured, the residual chlorine, and subsequently the oxygen which had been produced were estimated. Using 83.5 c.c. chlorine and 4 c.c. water, quantities in the ratio $Cl_2 : 64H_2O$, practically no action was found to have taken place after exposure during a month to strong diffused daylight, and during a second month to the direct action of tropical sunlight; but, the ratio being $Cl_2 : 88H_2O$, about 29 per cent of the chlorine was found to have been active, 6.5 c.c. of oxygen being liberated. Supposing action to have taken place according to the equation $2H_2O + Cl_2 = O_2 + 4HCl$, 7 c.c. of oxygen should have been obtained, an indication that a very small portion of the chlorine had undergone oxidation. The general result of a number of experiments of this kind was that, even in very strong tropical sunlight, water and chlorine interact to but a very slight extent when there are about 100 times as many molecules of water present as of chlorine; when the proportion is about $150H_2O : Cl_2$, action takes place to the extent of perhaps nearly 50 per cent of the possible amount; and, when more than $400H_2O : Cl_2$, interaction takes place much more rapidly, but even then only to about four-fifths of the theoretically possible extent. As the proportion of water is increased, the amount of chlorine which is oxidised becomes somewhat larger.

Chlorine-water saturated at $30-32^\circ$, the average working temperature in a Calcutta laboratory, contains chlorine in about the ratio $708H_2O : Cl_2$. Experiment shows that, when exposed to direct tropical sunlight, such water undergoes decomposition practically entirely in the sense of the equation $2H_2O + 2Cl_2 = O_2 + 4HCl$, an exceedingly small amount of chloric acid being formed. On exposing it to strong diffused daylight inside an open south verandah, either hypochlorous or chloric acid, or both, were formed in somewhat variable amount, the proportion of oxygen being much below that obtained in the previous experiments in bright sunlight. On exposing the chlorine-water to very moderate diffused light opposite the window in a room having a north light, very little, if any, oxygen was liberated, but the chlorine became oxidised to hypochlorous and chloric acids. In no case could chlorous acid or hydrogen peroxide be detected.

On exposing dilute solutions of hypochlorous acid to light, it was found that both oxygen and chloric acid were produced, the proportion of oxygen being larger the greater the intensity of the light. Solutions of chloric acid underwent little or no change.

The author concludes that in its first stages, at all events, the action of chlorine on water is quite similar to that which it exercises on dilute cold solutions of sodium and potassium hydroxides; and that in the subsequent stage it is very similar to that effected in the case of more concentrated and hot solutions of the two hydroxides.

30. "Note on the Explosion of Hydrogen Sulphide and of Carbon Bisulphide with Air and Oxygen. By Professor A. PEDLER.

The author finds that when a mixture of hydrogen sulphide, air, and oxygen is exploded, a normal result is obtained, sulphur dioxide and water being formed. But when carbon bisulphide vapour is similarly treated, a not inconsiderable proportion of the nitrogen of the air becomes oxidised; and after the explosion contraction continues to take place, owing to the formation of sulphuric compounds (chamber crystal, &c.) under the combined influence of the moisture present and the oxide of nitrogen. The results of a large number of experiments are described, showing the effect of various proportions of oxygen and air.

31. "The Action of Light on Phosphorus, and on Some of the Properties of "Amorphous" Phosphorus. By Professor A. PEDLER.

As part of an extensive series of experiments on the action of strong light on substances, the author has studied its effect on phosphorus, and has thereby been led also to examine and compare the several forms of allotropic phosphorus, viz., that produced by the action of light only, that produced at moderate temperatures, the commercial form, and also rhombohedral or metallic phosphorus prepared by dissolving phosphorus in lead at high temperatures.

The conclusion is arrived at that the term "amorphous phosphorus" is a distinct misnomer, and that, so far from commercial "amorphous" phosphorus constituting a separate allotropic modification of the element, it is in reality the same substance as the form called rhombohedral or metallic phosphorus, the very slight differences in character noticed between the substances in question being explained by the difference in the state of division and the slight variations conditioned by their mode of formation. Whether the term amorphous phosphorus can be truly applied to the forms made by the action of light is open to grave doubt; even in this case there appears to be distinct evidence of crystalline form, although, in some instances, a form which appeared to be amorphous was obtained. It is suggested that it would be better to altogether discard the use of the term *amorphous phosphorus*.

The author finds that when phosphorus is exposed to light in contact with liquids containing oxygen, such as alcohol, it tends to enter into action with them. He arrives at the conclusion that neither *in vacuo* nor at ordinary pressures is there any change whatever of red into ordinary phosphorus at 260° as ordinarily stated; and that, practically, no change occurs up to temperatures of nearly 358°, above which, *in vacuo*, change takes place, but exceedingly slowly, even up to 445°. He also describes experiments which tend to show that red phosphorus is not permanent in air, as commonly supposed.

32. "The Action of Phosphoric Anhydride on Fatty Acids." By F. S. KIPPING, Ph.D., D.Sc.

In a previous preliminary note (*Chem. Soc. Proc.*) the author has described the formation of the ketone stearone by the action of phosphoric anhydride on stearic acid; he now gives a detailed account of his experiments with this acid, and also describes the application of the same method to the preparation of dihexyl ketone, $(C_6H_{13})_2CO$, from heptylic acid. Two experiments gave 33 and 25 per cent respectively of the theoretical amount of dihexyl ketone; the yield of stearone being 40–42 per cent of the theoretical.

Dihexyl ketone is found to have the properties already described by Uslar and Seekamp (*Annalen*, cvi., 179). Its hydroxime and hydrazone were both obtained as yellow oils. Dihexyl carbinol was prepared by adding a large excess of sodium to an ethereal solution of the ketone placed in a flask, together with moderately concentrated soda solution; it crystallises from dilute alcohol in plates melting at 41–42°.

NOTICES OF BOOKS.

Pictorial History of Ancient Pharmacy, with Sketches of Early Medical Practice. By HERMANN PETERS. Translated from the German, and revised, with numerous additions, by Dr. WILLIAM NETTER. Chicago: G. P. Engelhard and Co. 1889. 8vo., pp. xiv.—184. Illustrated, cloth.

THOUGH ostensibly a work on pharmacy, these chapters of history contain much information on matters pertaining to chemistry in its early phases. The volume is not merely a translation of Mr. Peters' "Aus Pharmaceutische Vorzeit," as the American editor has added many features of especial interest to English readers, and has re-written some of the chapters in the light of researches not pursued by Mr. Peters. Professional chemists and pharmacists will find this well illustrated work a mine of information, the materials having been gathered with much diligence from sources not readily accessible. Chapter I., Tutelar Gods and Patron Saints of Pharmacy, treats of the myths of ancient Greece, and of medicine and surgery in symbolism. Chapters II. to V. treat of Pharmacy from the middle ages to the eighteenth century among the Chinese, Egyptians, Germans, and Anglo-Saxons, with sketches of the laws enacted at different periods, and notices of early literature. Chapter VI. deals with Distilling Apparatus in its various forms, and the next chapter with Early Chemo-Pharmaceutical Stoves and Fire-places. Chapter VIII. discusses Ancient Pharmacopoeias. Chapter IX., Medical Superstitions. Chapter X., Pharmacy and the Art of Love. Chapter XI., Alchemy.

As may be judged from the variety of topics here named, the author has not attempted to be exhaustive in each chapter, but in writing on alchemy and medicine he has ever borne their pharmaceutical bearings in remembrance. Chapter IX., on Medical Superstitions, is not so full as the well-known work of Dr. Pettigrew, yet it supplements the latter by contributing data from German sources.

The charm of this volume is, however, in its reproductions of old engravings, interior of chemist's shops ("drug-stores" in American English), portraits, facsimiles of title-pages of rare works, representations of ancient apparatus, and cuts of alchemical metaphors, gleaned from original sources. Not every student of chemistry is the owner of an alchemical library, and few have the time to search the shelves of great libraries for the quaint and curious publications of the sixteenth and seventeenth centuries; therefore this volume places in his hands a choice selection of the most interesting plates, with explanatory text, at a very moderate cost. We note the rude cut of a chemist's shop, dated 1450, another of 1536, and another of 1733, quite elaborate in decorations. We note the facsimile of a journeyman's certificate, 1743, and several reproductions from Maier's "Atalanta Fugiens," 1618, much prized by bibliophiles.

The author states that prominent among the early Virginian colonists was the surgeon and apothecary Dr. Edward Heldon, who had been a friend and pall-bearer of Shakespeare. The first shop distinctively devoted to pharmacy in Boston was opened, in 1646, by William Davies. The first patent medicine was called "Tuscarora Rice," sold as a consumption cure by a Mrs. Masters in 1711. Adulteration began to be practised quite early in New York, coloured sawdust having been sold for rhubarb. In the chapter on alchemy the translator adds some information of Peter Woulfe, of Barnard's Inn, one of the last of English believers in the hermetic art, and states that as recently as 1880 an American named Wise duped a member of the Roban family (a collateral descendant of the "necklace cardinal") by pretending to make gold. Wise secured a large sum of money and then disappeared.

In the first paragraph of Chapter XI. the author quotes

appropriately Mr. Crookes's address before the B.A.A.S., with reference to the evidence of the decomposition of the elements afforded by the aid of spectrum analysis.

The work seems to have gained rather than lost by the translation; we hope the translator will be encouraged to do as well for Peters's "second series," recently published, as he has for the first.

H.C.B.

A Technological Dictionary of Insurance Chemistry. By W. A. HARRIS, F.R.S.S.A., F.S.S., Phoenix Fire Office Liverpool.

NOT much reflection will be needed to convince our readers that chemistry has much light to throw upon fire insurance. In the absence of chemical knowledge it is impossible to decide what substances are dangerous, *per se*, or in contact with other bodies, or under special conditions of temperature or moisture. To supply such information has been the author's object. He has set himself "the task of endeavouring to find a royal road to an accurate estimation of the various forces at work in the creation of heat, fire, and explosion." This task he has executed very judiciously and successfully. He has rejected chemical formulae, which, invaluable as they are to the professional student, are simply an encumbrance to persons who are concerned merely with results, without reference to the processes by which they have been reached.

We find here information of a novel and startling character, but, as a rule, unexpected as the author's conclusions often are, we cannot pronounce them out of the question. In some instances, however, we find substances or manufacturing processes set down as dangerous when both theory and experience inform us to the contrary. Thus the manufacture of albumen—egg or blood—is said to be "of a very hazardous character." Now, we must point out that both the raw materials, the finished products, and any refuse are exceedingly combustible, and, from their non-porous character, incapable of absorbing and condensing gases and vapours. The temperatures used in the operation are, of course, exceedingly low.

On the other hand, that certain manures—dung-hills, stable manure, sewage manures, &c.—being of a fibrous or pulverulent texture, are liable to heating, need not be wondered at. The heat may, perhaps, rarely, if ever, rise to what is commonly known as combustion, but it often reaches a point which deteriorates the manure. Repeated attention is drawn to the danger of organic dusts of various kinds, which, if diffused in common air, may even form very dangerous explosive mixtures. Still less are the public alive to the fact that substances which when dry are perfectly safe may become capable of what is known as spontaneous combustion if slightly damp. It is, we believe, on record that conflagrations are most frequent and most destructive in damp weather.

The author further calls public notice to the neglected fact that wood-work which has for a long time been exposed to temperatures not exceeding that of boiling water undergoes a chemical change and becomes dangerous. Thus beams which have been in contact with steam or hot water pipes have been found charred to some depth. The obvious inference is that such pipes should be made to rest upon incombustible matter only.

The dangers of cotton-waste moistened with oil and allowed to lie in a neglected corner are repeatedly enforced. The number of factories which are burnt down from neglect of this kind is very serious.

Cases are given of accidents from the use of saw-dust to soak up spillage of oils, glycerin, &c. It may also fire if injudiciously mixed with certain acids or salts. Indeed, it should always be looked upon with suspicion, and never let lie in works or warehouses.

Many errors may be found in this work, but as they have no direct bearing on the author's subject they do not

need to be specified. Thus, whether a dye-wood is obtained from India or South America does not affect its dangerous character when finely ground, moistened, and allowed to lie in heaps.

When, however, we remember that water-gas contains from 30 to 40 per cent of carbon monoxide, we cannot help admiring the rashness of the medical men at Boston who have asserted that this mixture is not more dangerous to health than coal-gas.

A little expected, though perfectly conceivable, source of danger is mentioned as existing in leaden roofs and gutters. A deposit is formed which seems capable of igniting in a current of air, and of then setting fire to combustible materials.

The part played by rats in occasioning unaccountable conflagrations is not overlooked. These vermin, it appears, have developed a taste for lucifer matches, which they carry off to their holes and leave in contact with pilferings in the shape of tallow, fragments of paper, &c. It would be wise to allow no matches on ship-board or in warehouses except in iron boxes.

Celluloid is not without its perils. A comb made of this material is said to have become ignited from exposure to a heat of 180° F. As it was at the moment fixed in the hair of a little girl, who was sitting before the fire, the consequences were highly unpleasant.

This work is one of great value not merely to fire insurance companies and their officials, but to manufacturers, warehousemen, shippers, and sea captains, who may derive from it some most important lessons. Even the general public is concerned, as it may be seen from truths brought into prominence in the introduction. Our total national loss from fires is estimated at fourteen millions sterling yearly! Ten millions are annually paid by British insurance companies, and the remaining four millions will not do more than cover the loss on uninsured property. The world's total loss is estimated at sixty-seven millions! This fearful waste, as the author shows, is largely preventible. Hence we think that a debt of gratitude is due to him for the cautions which he gives in so plain and intelligible a manner.

A Treatise on Chemistry. By Sir H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Vol. III. The Chemistry of the Hydrocarbons and their Derivatives; or, Organic Chemistry. Part II. New and thoroughly Revised Edition. London and New York: Macmillan and Co., 1890.

THE present edition of this work has been very thoroughly revised. Much novel matter, as it is pointed out in the Preface, has been introduced, and the derivatives of furfuran, pyrrol, and thiophene will be described in a future volume, along with the derivatives of pyridene and quinoline. The work in its present form displays the thoroughness which won for the former edition such general approbation. Constant and abundant reference is made to the original memoirs used in compilation.

Under Tartaric Acid we find mention of the treatment which Scheele's first scientific paper underwent. Bergman, who had undertaken to lay the memoir before the Stockholm Academy, neglected so to do, and when Scheele rewrote the paper and entrusted it to the Secretary of the Academy, Retzius, the latter edited it in such a manner that much of the credit of the investigation seemed due to him.

We find no mention of any method of distinguishing beet-sugar from cane-sugar. Experienced merchants are said to discriminate between them by taste, and bees are certainly able to do the same, and reject beet-sugar if the product of the cane is accessible. This probably depends on the presence of traces of impurities, which, in practice, are never entirely eliminated.

Speaking of the deplorable explosion of gun-cotton at Stowmarket, in 1871, the authors say that "some of the stock of gun-cotton contained acid, owing either to in-

sufficient washing or to the felonious addition of acid to the properly washed gun-cotton." The facts ascertained during the enquiry, we should submit, entirely eliminate the former alternative. In each of a number of cases which had been sent to Upnor Castle a couple of days before the explosion one disc of discoloured gun-cotton was found, evidently in course of decomposition. The rest of the contents of the cases were sound. Had the cotton been imperfectly washed traces of decomposition would not have been confined to single discs.

The index is very extensive, and, as far as we have been able to test, singularly correct.

CORRESPONDENCE.

VOLUMETRIC ANALYSIS OF COPPER.

To the Editor of the Chemical News.

SIR,—I am glad to see a note on the "Volumetric Analysis of Copper" by Mr. R. A. Fessenden in the *CHEM. NEWS*, vol. lxi., p. 183, and that he advocates the use of sodium carbonate instead of ammonia in a solution to be titrated by cyanide of potassium. The writer did the same in the *CHEM. NEWS*, vol. lviii., p. 131, and is pleased to see the confirmation of Mr. Fessenden.—I am, &c.,

J. L. DAVIES.

Hafod Isha Works, Swansea.
April 23, 1890.

MILK ANALYSIS.

To the Editor of the Chemical News.

SIR,—I have read Mr. Walls' article on "Milk Analysis" in the *CHEM. NEWS*, vol. lxi., p. 162. Essentially, the same process was described by me on May 27th, 1887, in a paper read before the Royal Society of Canada, of which I enclose a copy. The method "hat sich bewährt," as the Germans say, is always employed here, and has been adopted in some other laboratories. The asbestos fibre used is that produced largely in Canada, and is really asbestiform serpentine or crysotile.—I am, &c.,

THOMAS MACFARLANE
(Chief Analyst I. R. D.).

Laboratory of the
Inland Revenue Department.
Ottawa, April 15, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 15, April 14, 1890.

Artificial Production of Silk.—Emile Blanchard.—The writer suggests the possibility of obtaining silk by an artificial digestion of the leaves of the mulberry, followed by dialysis. He does not come to any definite conclusion.

Action of Nitric Acid upon Aluminium.—A. Ditte.—Both with dilute nitric and sulphuric acid the metal becomes covered with a gaseous stratum which prevents its contact with the acid. If the experiment is prolonged for some days bubbles of gas are slowly formed upon the metal, which dissolves little by little. In a vacuum the action is more rapid. There is no liberation of hydrogen; in very dilute nitric acid there is given off a mixture of nitrogen and nitric oxide, the former predominating,

whilst ammonia remains in the liquid. All these reactions are exothermic, and sometimes one of them is produced almost exclusively. In a vacuum the nitric acid is converted into neutral aluminium nitrate; but the reaction does not then stop, as the nitrate, like the sulphate, is attacked by aluminium, and a sub-salt is formed. If aluminium is heated in a solution of its nitrate bubbles of hydrogen are given off, and if the heating and the concentration of the liquid are kept constant there appears a white granular precipitate of basic nitrate.

Preparation of Hydrobromic Acid.—A. Recona.—The author causes sulphuretted hydrogen, furnished by a continuous apparatus, to pass through bromine in a tall narrow bottle, surmounted by a stratum of water, or preferably of hydrobromic acid. The gas which issues from this bottle, which is hydrobromic acid, traverses a second bottle containing a solution of potassium bromide, holding a little red phosphorus in suspension. This second bottle entirely arrests all vapours of free bromine escaping from the first bottle. The gas given off does not contain a trace of hydrogen sulphide, and is always pure hydrobromic acid, however rapid the current.

Oxidation of Hypophosphorous Acid by Palladium Hydride in the Absence of Oxygen.—R. Engel.—Palladium hydride determines the oxidation of hypophosphorous acid, yielding phosphorous acid and liberating hydrogen. The hydride seizes an atom of the hydrogen of the hypophosphorous acid and gives it up again immediately in the free state. The residue of the hypophosphorous acid completes its molecule by decomposing water, fixing hydroxyl, and liberating a further atom of hydrogen. The action seems to continue indefinitely. With 0.5 grm. of palladium hydride the author has decomposed the phosphorous acid from 500 grms. barium hyposulphite without any decrease in the activity of the precipitate.

Oxidising and Decolourising Properties of Charcoals.—P. Cazeneuve.—If the decolourising properties of charcoals are chiefly due to a mechanical fixation of the colours upon the carbonaceous matter, we must not overlook the action of the oxygen condensed in the pores in a state comparable to ozone. This oxygen has a destructive action upon certain colours, whilst, on the contrary, it determines the appearance of others which are products of oxidation.

On the Camphoric Acids.—E. Jungfleisch.—A study of the solubilities of ordinary dextro-camphoric acid, of the levo-camphoric acid of *Matricaria*, and of the levo-acid of transformation.

On Potassium Malonate, Quadromalonate, and Quodroxalate.—G. Massol.—A thermo-chemical paper which does not admit of useful abstraction.

Extraction of Raffinose from Molasses. Separation of Raffinose and Saccharose.—L. Lindet.—Four successive operations are necessary for the extraction:—(1) Purification and decolouration of the molasses by means of mercury sulphate, baryta, and methylic alcohol. (2) Dehydration of the methylic solution by means of lime at the boiling-point of methylic alcohol. (3) Precipitation of the methylic solution by ordinary alcohol. (4) Crystallisation of the precipitate in ethyl alcohol at 80–85°.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6

Determination of Traces of Iron in Alums and Aluminium Sulphate.—R. R. Tatlock.—From the *Journal Soc. Chem. Industry*.

Determination of Gallium.—Lecoq de Boisbaudran (*Annales de Chimie*) calls attention to the volatility of gallium chloride, Ga_2Cl_6 , which occurs even in the evaporation of hydrochloric solutions. If sulphuric acid is added to the hydrochloric solutions no loss of gallium

occurs, even on heating the residue to dull redness. In evaporating hydrochloric solutions of gallium chloride in quantitative investigations, apparatus must be used which permits of condensation of fumes. The best absorbent is potassium-lye.

Method for Separating Gold, Platinum, Antimony, Arsenic, and Tin.—M. Silva (*Bull. Soc. Chimique de Paris*), MM. Dirvell and Bricout (*ibidem*) and Ad. Carnot (*Comptes Rendus*).—Already noticed.

Determination of Arsenic in Pyrites.—John Clark.—From the *Journ. Soc. Chem. Industry*.

Determination of Arsenic in Metallic Copper.—J. Clark.—From the same source.

Volumetric Determination of Phosphorus in Iron and Steel.—E. D. Campbell.—From the *Journal of Analyt. Chemistry*.

Detection and Determination of Iodine, Bromine, and Chlorine.—M. Dechan.—From the *Journal of the Chem. Society*.

Theophylline.—A. Kossel (*Ber. Deutsch. Chem. Gesellschaft*).—A base obtained from the extract of tea, $C_7H_5N_3O_2 + 2H_2O$, but distinct in properties from its isomers theobromine and paraxanthine. It is soluble in water, alcohol, and ammonia; it melts at 264° . It forms with hydrochloric acid, sulphuric acid, gold, and platinum chlorides, definitely crystalline salts, and with mercuric chloride a crystalline sparingly soluble double salt. If theophylline is evaporated with chlorine-water it gives a scarlet residue, passing into violet on the addition of ammonia. Theophylline is converted into caffeine by the introduction of a methyl-group.

Imperialine.—K. Fragner (*Ber. Deutsch. Chem. Gesells.*).—Already noticed.

Reactions of a Number of Alkaloids, Glycosides, and Kindred Bodies with Sulphovanadic Acid.—F. Kundrat.—Already noticed.

Reaction for Acetanilide.—M. Denigès (*Soc. Pharm. Bord. per Chemiker Zeitung*) points out that acetanilide, like all anilides, if boiled with an alcoholic solution of sodium hypobromide, gives an orange precipitate, and evolves a distinct odour of methyl cyanide.

Corresponding Reactions of Carbazol and Pyrrol.—S. C. Hooker.—Already inserted.

Reactions of Some Phenols and Analogous Bodies with Chloroform and Alkalies.—G. A. Raupenstrauch (*Soc. Pharm. Bordeaux and Chemiker Zeitung*).—The coloured reaction which occurs in the action of chloroform and the alkalies is characteristic for all phenols and phenoloid bodies, and does not, therefore, at once indicate the presence of any given body. The author boiled 2 c.c. of a solution of 1 part of a phenol in 1000 parts of chloroform in a test-tube with a fragment of caustic potassa and diluted to the margin of visibility. Carbolie acid gave a pale red tinge at 1 in 60,000; orthokresol a lilac at 1 : 80,000; meta-kresol more inclining to orange at the same dilution; thymol, a splendid purple red with a violet cast, 1 : 20,000; guajacol, cherry-red with a blue cast passing into violet blue, 1 : 100,000; resorcin, 1 : 500,000; β naphthol, prussian blue passing into green and brown up to 1 : 80,000; salol gives the same colouration as carbolie acid; betol the same as naphthol; potassium-hydroxide gives more intense colours than sodium hydroxide. In many cases alcohol and ether prevent the reaction. For detecting the phenols in other bodies (the contents of the stomach, in medicines, blood, urine) the author acidulates with dilute sulphuric acid and distills in a current of steam. The first drops which pass over generally contain the phenol. It is shaken up in a parting funnel with 5 c.c. chloroform; the latter is separated from the watery liquid and heated with a fragment of potassa. If the liquid contains alcohol it is first rendered alkaline, the alcohol is distilled off, the residue is acidified, and treated as above. The reaction

may be used for recognising chloroform, chloral, or iodoform.

The Distinction of Resorcin from Carbolie and Salicylic Acids.—H. Bodde.—From the *Analyst and Nederl. Tijdschrift Pharmacie*.

Coloured Reactions and Aldehydic Character of Woody Fibre.—E. Nickel.—No particulars are given.

Detection of Saccharine (Benzoic Sulphinide).—B. Haas (*Chemiker Zeitung and Deutsche Chemiker Zeitung*).—The author condemns the method of Bornstein and gives the preference to the method of Schmitt.

Detection of Chlorine, Bromine, Iodine, and Sulphur in Organic Matter.—C. W. Marsh.—From the *American Chemical Journal*.

Determination of Carbon and Hydrogen by Combustion.—W. L. Dudley.—From the *American Chemical Journal*.

Determination of Tannin.—M. Counciler and Von Schröder.—A reply to the objections urged against the author's method by Simand. The necessity of operating in dilute solutions is shown. The method is, in many cases, preferable to that of Löwenthal, e.g., in the case of extracts of pine-bark.

A New Form of the Hide Filter.—L. Schreiner (*Gerber*).—The apparatus is shown in an accompanying cut. J. Meerkatz has found it possible to use the gravimetric process for determining tannin in acid liquors by previously neutralising with barium carbonate.

Detection of the Elements of the Tissues of Wheat and Rye-Meal.—P. Soltsien (*Pharm. Zeitung*).—Already inserted.

Examination of Butter.—This bulky compilation does not admit of useful abstraction.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

A Supposed New Gaseous Element.—The *Chemiker Zeitung* gives an account of a discovery made in Damara Land which appears to be of profound interest. A mining engineer of the name of Lauer, prospecting for gold, came upon a group of funnel-shaped depressions in a tract of weathered diabase. Whilst the ground was elsewhere of a reddish colour (from ferric oxide), in the immediate neighbourhood of these depressions it was of a greenish-grey. There was not a trace of even the lowest vegetation; dried insects and the remains of antelopes, jackals, and lizards, all displayed a remarkable change of colour. One of the party had in his hat a branch of a shrub, which in a very short time lost its green colour and assumed a violet blue, whilst the beads and hair of the travellers appeared as if powdered over with white. A peculiar odour was perceived, intermediate between musk and mercaptan, and on bending down over the fumaroles a slight humming sound was perceived. Three empty bottles were filled with the gas and forwarded to Dr. Antsch, a chemist residing at Cape Town. The latter assigns to this gas the provisional name damarium (D). It is capable of decomposing water and taking the place of the hydrogen. Its combination with oxygen, on electrolysis, evolved at the positive pole a volume only one-fourth of that given off at the negative pole. The latter has exactly half the specific gravity of H, and its oxide has the composition D_2H . D is therefore semivalent, or, more correctly, it is the true univalent element of the lowest atomic weight, and must in future be placed at the bottom of our atomic scale. H, Cl . . . must in future be regarded as bivalent; O, S, &c., as quadrivalent. The stereo-chemical view of Le Bel and van't Hoff thus receives a severe blow, and the "tetrahedric representation" becomes impossible. Damarium is the most powerful of all reducing agents. Platinum, gold, silver, lead, and copper are at once reduced from their solutions in the metallic state; ferric salts are reduced in a moment to ferrous salts, and mercuric chloride is converted into calomel. Solution of indigotine is instantly decolorised, and nitrobenzol is converted into aniline. Damarium rapidly separates sulphur from the aqueous solution of SO_2 , and if passed through dilute sulphuric acid it causes an escape of sulphuretted hydrogen. Dr. Antsch, who is intending to prosecute the investigation on the receipt of further material, is of opinion that damarium is an element, perhaps widely diffused, but generally occurring in very minute quantities, and hence hitherto overlooked. Its concentrated occurrence in Damara Land is analogous to the occurrence of the cerium metals.

MEETINGS FOR THE WEEK.

- MONDAY 5th.**—Medical, 8.30. (Annual Oration).
 — Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
 — Society of Chemical Industry, 8. "The Dunsmuir Process," by Watson Smith. "Some Considerations in the Chemistry of Bleaching," by Messrs. Cross and Bevan. "Mixture in Paper Pulp," by M. L. Griffin.
 — Royal Institution, 5. General Monthly Meeting.
TUESDAY, 6th.—Royal Institution, 3. "The Art of Engraving—1. Line Engraving," by Louis Fagan.
 — Institute of Civil Engineers, 8.
 — Pathological, 8.30.
WEDNESDAY, 7th.—Society of Arts, 8. "The Aim and Scope of Higher Technical Teaching," by Dr. Percy F. Frankland.
THURSDAY, 8th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
 — Society of Arts, 5. "The Western Frontier of China," by Demetrius Boulger.
 — Society of Arts, 8. "Design Applied to Wood-carving," by Lewis F. Day.
 — Royal, 4.30.
 — Chemical, 8. (Extra Meeting). Exhibition of Apparatus, &c.
 — Institute of Electrical Engineers, 8.
 — Mathematical, 8.
FRIDAY, 9th.—Royal Institution, 9. "Colour-vision and Colour-blindness," by R. Brudenell Carter, F.R.C.S.
 — Quekett Club, 8.
 — Astronomical, 8.
SATURDAY, 10th.—Royal Institution, 3. "Recent Excavations in Greece," by Dr. Charles Waldstein.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1589.

THE RAPID ESTIMATION OF ARSENIC.

By F. W. BOAM, F.C.S.

THE author having occasion to estimate the amount of arsenic (equal to As_2O_3) in a large number of samples of its ores, it became of importance to obtain a quick and accurate method for its determination. The usual known "magnesia" and "uranium acetate" methods are lengthy and require the greatest care in order to be accurate. The "iodine" method, though accurate and quickly performed when employed for "refined white arsenic," is very lengthy and bothering when applied to arsenical ores, and affords several opportunities for error during the preparation of the test solution for titration! Such being the case, the author was led to experiment upon the following modification of the "uranium acetate" method:—

About 1 to 1.5 grms. of the ore, previously dried at 100° and powdered, is taken and boiled to dryness with 20 to 25 c.c. pure strong HNO_3 . When cool, about 30 c.c. strong $NaHO$ solution (30 per cent) are added and boiled for a short time, and the liquid filtered off and diluted to 250 c.c. 25 c.c. of this solution are taken, made acid with a ten per cent solution of sodium acetate, in 50 per cent acetic acid, and the mixture boiled. It is then titrated with a quarter normal solution of uranium acetate (made by dissolving 17.1 grms. uranium acetate in 15 c.c. strong acetic acid, and diluting to 2 litres), 1 c.c. equalling 0.00125 gm. As . A solution of K_4FeCy_6 "spotted out" on a white tile is used as the indicator; a drop of the test solution giving a reddish brown colouration with this when the titration is finished.

This method is applicable to all ores containing arsenic, and which are attacked by HNO_3 . The author has fully tested it against other methods and finds that it holds the palm for rapidity and accuracy. A sample of "arsenical iron pyrites" can be analysed by its means in less than two hours. The difficulty at first met with in employing this method is a tendency to form an insoluble unstable arseniate of iron upon adding the $NaHO$ solution, but the author finds that by employing a moderately strong solution of $NaHO$ in excess, and boiling, this compound is decomposed, whereby the hydrate of iron can be filtered off without loss of arsenic.

Coombe Arsenic Works,
Callington, Cornwall.

ODORISING WATER-GAS.

By Dr. J. LEWKOWITSCH, F.I.C., F.C.S.

THE serious dangers attending life through an unobserved escape of water-gas have led many experimenters to impart to this gas a volatile substance the odour of which would readily indicate the presence of water-gas in the air. All attempts in this direction proved hitherto fruitless, even mercaptan not being adapted for this purpose, as last year's sad occurrence in the Leeds Forge proved.

About that time Baumann published in the *Berichte* (1889, p. 2593) his paper on thio-acetone, and quite naturally it occurred to me that this substance, the powerful odouring properties of which Baumann described in such a vivid manner, might perhaps be usefully applied to the odouring of water-gas.

A few experiments satisfied me that it would be comparatively easy to prepare this substance for the said purpose, especially as it would not be required to prepare a

chemically pure substance, any larger amount of the polymers not being objectionable at all.

I communicated afterwards with the British Water-Gas Syndicate in this town, and the necessary experiments were carried out in the chemical laboratory of the Leeds Forge. Owing to the pressure of other important work and a serious illness, the final experiment, *i.e.*, the admixture to the water-gas, has not yet been carried out.

The substance in question possesses, as was to be expected according to Baumann, a most powerful odour, causing at the same time sickness and headache, when the vapours are highly diluted, *e.g.*, with air. While preparing this thio-acetone one does not meet with very great inconvenience, at least, not greater than experienced when working on similar substances. There is a very curious analogy between the odouring properties of this thio-acetone and other substances of great scenting power, for instance, otto of roses—of course, in a very opposite direction as far as the pleasantness is concerned. The pure rose oil has only a faint and, perhaps, not agreeable smell, but in very dilute solutions the lovely scent is brought out. Similarly, the fearful smell of the thioacetone is brought out when it is diluted with large quantities of air. I had for this a very serious—although at the time a very welcome—confirmation. While distilling the product of the reaction of sulphuretted hydrogen on about 20 grms. of acetone, two workmen, working at the opposite end of the steel works, entered the laboratory complaining of the fearful smell, and declaring that they had been vomiting, felt altogether sick and unable to continue their work.

In conclusion, I wish to point out that acroleine would lend itself admirably to this purpose, as I may conclude from the complaints I had some years ago, caused by very minute quantities of acroleine escaping from the glycerin distilling of the undermentioned works. Experiments on the use of acroleine are being carried out at present. The absence of sulphur in it would recommend it all the more

Whitehall Soap Works, Leeds.

A FUNDAMENTAL PROPERTY COMMON TO BOTH CLASSES OF SPECTRA. DISTINCTIVE CHARACTERS OF EACH CLASS. PERIODIC VARIATIONS WITH THREE PARAMETERS.

By H. DESLANDRES.

M. RYDBERG has recently submitted to the Academy a very interesting study on the succession of vibratory periods in line spectra. He set out from the anterior researches of MM. Lecoq de Boisbaudran, Mascart, Liveing and Dewar, and Cornu and Balmer, and condensed the facts established in certain simple laws.

The author has studied the other class, the band-spectra, from the same point of view, and has proposed two simple laws for the distribution of the rays and the bands. It is convenient to bring them forward anew, but under a form analogous to that adopted by M. Rydberg for the line-spectra. The comparison between the two classes of spectra will thus be rendered easy; it will bring into prominence, on the one hand a fundamental property which is common to both, and on the other the characters peculiar to each class.

Line-Spectra.—The laws of M. Rydberg apply to the bodies which constitute the three first families of Mendeleeff, that is almost all the metals. In these substances the long rays (which are the most important and even the only ones of the electric arc) form groups of two or three rays (doublets or triplets) which succeed each other at regularly decreasing intervals, so as to form series having the same aspect for all bodies.

In the scale of number of waves or of vibrations in

each series the corresponding rays of the doublets or triplets are represented by a function of the whole numbers of the form—

$$N = A - \frac{\alpha}{(m + p)^2}$$

N being the number of waves, A, α two constants, μ a constant < 1 , m a whole number. This function has, as its limit, the simplest function—

$$N = A - \frac{\alpha}{m^2}$$

which, for the suitable values of A and α , represents exactly, as was first shown by Balmer, the simple series of the simple rays of hydrogen.

Band-Spectra have given rise to less research than the former, as they are less intense, less easy to produce, and they require a very powerful dispersion. The author has studied at least 12 distinct band spectra, some having more than 40 bands (*Comptes Rendus*, 1886 and 1887). They are due to the non-metallic bodies.

They have one point in common with the line spectra. Any band whatever, with a sufficient dispersion, seems formed by similar groups of one, two, or three rays, or even more, which follow each other at regularly variable intervals. All the bands of one and the same spectrum are similar, and are formed by the same groupings. This structure of similar groups is a fundamental property common to all spectra.

But the distribution of the groups is here different. It is represented for one band by the function $N = A + \alpha m^2$, m being a whole number and A and α two constants. For increasing values of m the intervals increase (even in arithmetical progression), whilst the line spectra decrease progressively.

Further, as a spectrum usually comprises several bands, the general law of distribution must be more complex. The author has shown that in the scale of wave-numbers the complete series of similar groups may be represented by a function of three variable parameters,—

$$m_1 n_1 p - N = f(n_1^2 p^2) \times m^2 + B n^2 + \phi(p^2);$$

$m_1 n_1 p$ being the values of whole numbers, B being a constant, f and ϕ simple functions, the study of which is not yet completed. The function N has three parameters, but in some spectra it is reduced to two or even to one.

This distribution to the dependence of three parameters is a characteristic of band spectra in contradistinction to line-spectra which are governed by a single parameter.

As to the nature of the grouping of the similar rays, the repetition of which forms spectra, it has the same importance in both classes. As in the metallic spectra, there are differences between substances of different families. Thus carbon presents a series of doublets with three parameters, oxygen a series of doublets with two parameters, nitrogen a series of triplets with three parameters, and a series of simple rays having three parameters.

But the occurrence in the spectra of series of rays of three parameters is not surprising. We find in general three groups of periods and three parameters in the problems of periodic variations in which the three dimensions of space intervene; the three parameters corresponded exactly to these three dimensions. Thus, in the problem of the most general vibratory movement of a solid body theory distinctly indicates a total of periods assimilable to a table of three entries. We may affirm that the sounds or the shocks heard at any instant are most commonly complex sounds of three parameters. This character has not been recognised as yet because our senses and our means of investigation do not allow us to separate in the same time many sounds emitted simultaneously.

In optics the conditions are more favourable. The powerful dispersive apparatus at our disposal enables us to separate all the components of any vibration whatever, and to distinguish two neighbouring vibrations which

differ respectively by less than 1-100,000th of their number of waves. Thus the spectra of bands formed of very numerous and very approximating rays have been studied completely. These band-spectra form the first experimental verification of periodic variations with three parameters.—*Comptes Rendus*, cx., p. 748.

NEW METHOD FOR THE SEPARATION OF VANADIC AND TUNGSTIC ACIDS.

By CARL FRIEDHEIM.

THE following method gives trustworthy results:—

The concentrated solution of the salt is mixed in a capacious porcelain capsule on a boiling water-bath with a strong solution of mercurous nitrate, as neutral as possible, until the precipitate formed settles well, and then digested for about twenty minutes with an excess of freshly precipitated mercuric oxide, to neutralise the free acid. When cold, the precipitate—a mixture of the mercury salts of both acids with excess of mercuric oxide—is filtered through a smooth filter, washed with water containing a few drops of mercurous nitrate, which is quickly effected, then rinsed back as completely as possible from the filter into the capsule used for precipitation, and the contents of the capsule are evaporated to a paste. When cold, it is treated with an excess of the strongest hydrochloric acid, stirring carefully, and heated for five minutes upon a boiling water-bath, covered with a watch-glass.

All the vanadium dissolves as vanadyl chloride, almost all the tungstic acid and the bulk of the mercury dissolve also. The blue solution is mixed with much water, when the dissolved tungstic acid is thrown down almost quantitatively, whilst vanadium and mercury remain in solution.

The residue of the precipitate left on the filter is dissolved in hot hydrochloric acid, sp. gr. 1.12, and added to the solution. After twenty-four hours, the precipitate is filtered off, washed with water very slightly acidulated with hydrochloric acid, the residue adhering to the capsule is rinsed into a tared porcelain crucible with a little ammonia, the contents of the filter evaporated to dryness on the water-bath, the filter, still moist, is placed in the crucible, dried in the air-bath at 120°, and ignited with excess of air, at first under a draught-hood, on account of the mercuric chloride: there remains pure yellow tungstic acid. From the filtrate, after heating to 80°, the mercury is thrown down as sulphide by a prolonged introduction of hydrogen sulphide until the precipitate has completely deposited. The filtrate, containing vanadyl chloride, is evaporated to dryness on the water-bath, oxidised with strong nitric acid under a watch-glass on the water-bath, again evaporated, repeating the operation at least twice, and the brown hydrated vanadic acid dissolved in water with the addition of a few drops of nitric acid.

The solution is placed in a weighed platinum capsule, evaporated, the rest of the hydrated vanadic acid which has remained in the porcelain capsule is dissolved in a minimum of ammonia, added to the main quantity, again evaporated, dried at 120° in the air-bath, and then heated in the oxidising flame with excess of air (avoiding melting at first), and finally distributing the diffused mass over the sides of the crucible by agitation. The result contains only one-tenth to one-fifth per cent of the total quantity of WO_3 . To determine it, the contents of filter, after weighing, are treated with dilute sulphuric acid and sulphurous acid at a moderate heat, when all the vanadium is dissolved as vanadyl sulphate. The residue of tungstic acid, after filtration, is washed with very dilute sulphuric acid and weighed. The solution of vanadium is evaporated, the sulphuric acid driven off by heat, and

the residue ignited as above described, when perfectly homogeneous vanadic acid is obtained.

From the filtrate of the mercury salts of the acids the mercury is removed by sulphuretted hydrogen, and the alkali is determined as sulphate, the acid salts, as it is indicated by Krüss, being converted into normal salts by heating in a current of air charged with ammonia.

If the method is to be applied to meta-tungstates, they must first be converted into ordinary tungstates, by boiling and repeated evaporation in ammonia. The solution, freed from any excess of ammonia, is precipitated as described. Lead and silver salts are best decomposed by treatment with a very dilute alkaline hypochlorite, and the remaining metallic and earthy alkaline salts by repeated fusion with sodium-potassium carbonate; the united alkaline liquids are neutralised with acetic acid at a gentle heat and precipitated as directed. Extreme purity of all the reagents is indispensable.—*Berichte Deutsch. Chem. Gesell.*, vol. xxiii., p. 352.

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Continued from p. 217).

2. Detection and Determination of Arsenic.

If the absence of mercury and antimony has been decided, 50—100 c.c. of the liquid are tested directly for arsenic in the Marsh apparatus. Prominent attention must be given to the following points:—

1. The zinc to be used before being placed in the generating flask must be washed with hydrochloric acid, i.e., it must be exposed to the action of the acid for about ten minutes; the solution is then poured off, and the zinc is well washed with water. In this manner the traces of arsenic which often adhere to the zinc on the outside only can be removed.

2. In setting the apparatus in action the gas escaping at the aperture for exit must not be ignited until the operator has satisfied himself, by heating the reduction tube before the first contracted part, that all the atmospheric air has been expelled from the apparatus. In this manner the risk of explosion is avoided.

3. The liquid to be tested must be introduced into the flask in very small portions only, especially at first. In this manner the danger of frothing and running over may be avoided. If a deposit of arsenic appears in the reduction tube, the operator must always wait to see whether it visibly increases before adding a fresh quantity of the liquid.

4. The preparation of arsenical spots may be conveniently omitted, because it succeeds only when arsenic is present in considerable quantity and the escape of hydrogen arsenide is violent, which occasions a necessary loss of arsenic. The qualitative reactions of arsenic can be quite as well carried out with the "mirrors," which also serve better as exhibits than arsenical spots, which easily disappear if chlorine is present in the atmosphere.

If the quantity of arsenic present is not too small, and if it is practicable to obtain two mirrors, the reduction-tube is very carefully cut up with a diamond at its contracted portions, so that there result four pieces, each with half a mirror. With these mirrors the following tests are executed:—

1. One mirror is used for the odour test.
2. The second mirror is tested for its solubility in a freshly prepared solution of sodium hypochlorite.
3. The third mirror is dissolved in nitric acid and silver arsenite (or arseniate) is formed by adding silver nitrate.
4. The fourth mirror is oxidised with nitric acid, and converted into arsenic sulphide by treatment with colourless ammonium sulphide.

These four reactions will be in all cases perfectly satisfactory.

For the quantitative determination, sulphuretted hydrogen is passed into the hot solution for twelve hours; the flask is let stand, closely stoppered, for three to five days, until the precipitate has entirely settled, when the excess of sulphuretted hydrogen is expelled by a current of carbonic acid, and the precipitate is filtered off. A subsequent dulness in the filtrate, which was at first clear, cannot be avoided. The precipitate, consisting chiefly of organic matter, demands no further attention, since we have here to do with traces of arsenic which no longer admit of quantitative determination, as the last residues of arsenic can hardly be precipitated by means of sulphuretted hydrogen. Otherwise the procedure is similar to that described for antimony.

The following points must be remembered:—

1. The arsenic sulphide upon the filter must be dissolved only by means of ammonia or ammonium carbonate, as thus the sulphur present is least likely to pass into solution.

2. The fusion of the ammoniacal residue after treatment with nitric acid must be effected in a porcelain crucible with the readily fusible mixture of potassium-sodium carbonate and potassium nitrate.

3. The arsenic must always be weighed as magnesium pyro-arsenate.

4. A direct precipitation of the arsenic acid in the alkaline solution of the melt must be avoided. The arsenic must be again precipitated with sulphuretted hydrogen in the solution acidulated with nitric acid and freed from carbonic acid and nitrous acid; and after the arsenic sulphide has been converted into arsenic acid the latter, in a clear strong watery solution, must be precipitated with the mixture.

5. The precipitate of ammonium-magnesium arsenic must be re-dissolved in hydrochloric acid on the filter, and the solution again precipitated with ammonia. In this manner an excess of magnesia mixture is avoided, as well as the possible precipitation of magnesium hydroxide. The precipitate of ammonium-magnesium arseniate must be finely crystalline.

6. For converting the arseniate into pyroarsenate de Koninck recommends, when the quantity of arsenic is small, to dissolve the precipitate at once in water containing nitric acid, to evaporate down the solution in a small porcelain crucible on the water-bath, and to ignite the residue gradually and cautiously. By means of this improved method the author has lately succeeded in determining such small quantities of arsenic as 0.0003 to 0.0077 in the organs of dead bodies. A check experiment performed on the latter quantity in Marsh's apparatus gave five distinct arsenical mirrors.

7. Large quantities of magnesium pyroarsenate are preserved as exhibits; smaller quantities are converted into metallic arsenic in the Marsh apparatus, and the mirrors are sealed up.

b. Examination for other Metals, excepting Tin.

If the absence of mercury, antimony, and arsenic has been proved, the hydrochloric solution is put in a flask, rendered alkaline with soda-lye (free from alumina), acidulated with acetic acid, and treated with sulphuretted hydrogen, first at a boil and then until cold.

The contents of the flask are mixed with sodium carbonate until the reaction is distinctly alkaline, and left stoppered until quite clear. It is then filtered, the black precipitate, consisting, in ordinary cases, chiefly of iron sulphide, is drained and washed with a dilute solution of sodium sulphide containing hydrogen sulphide until the filtrate runs off colourless. The filtrate is set aside; the precipitate is put in a well-glazed porcelain capsule carefully oxidised with nitric acid, the evaporated residue is moistened with caustic soda (prepared from the metal), mixed with potassium sodium-carbonate, and the dry mixture is gradually introduced into melting saltpetre in

a silver crucible. In this manner, all organic matter accompanying the sulphides is completely got rid of. The melt is directly lixiviated in the silver crucible, the liquid is carefully supersaturated with hydrochloric acid and filtered into a beaker through asbestos (if manganates are present, otherwise through paper), to remove silver chloride, and the hydrochloric solution is further examined, qualitatively and quantitatively, according to ordinary analytical methods.

(To be continued).

ASH DETERMINATION IN RAW SUGARS.*

By F. G. WIECHMANN, Ph.D.

(Concluded from p. 212).

In order, however, that the determinations should be perfectly parallel, a separate estimation was made in each sugar of the inorganic suspended impurities, and the amount found deducted from the sulphate ash.

The following table exhibits the results obtained:—

Analysis number.	Sugar.	Polarisation.	Carbo-nate ash.	Sul-phate ash, —Yb.	Difference. The results obtained as sulphates are:—
1.	Dominica Muscovado.. ..	86.0	1.25	1.06	-0.19
2.	Java, 2nd product	86.5	1.32	0.99	-0.33
3.	" "	88.8	1.06	0.86	-0.20
4.	" "	86.3	1.05	0.79	-0.26
5.	" "	86.7	0.81	0.62	-0.19
6.	" "	87.5	1.26	0.92	-0.34
7.	Trinidad Concrete	84.0	2.47	2.08	-0.39
8.	Ilo-Ilo.. ..	86.6	1.91	1.42	-0.49
9.	" "	80.8	2.30	1.98	-0.32
10.	New Orleans Muscovado	91.2	0.76	0.49	-0.27
11.	New Orleans Muscovado	80.2	3.08	2.68	-0.40
12.	New Orleans Melado	79.1	1.69	1.19	-0.50
13.	New Orleans Melado	52.0	1.42	1.09	-0.33
14.	St. Croix Muscovado	88.0	1.27	1.04	-0.23
15.	Ceroons	83.8	1.78	1.25	-0.53
16.	Brazil	84.1	1.95	1.22	-0.73
17.	Java Stroops ..	77.4	4.16	3.72	-0.44
18.	Mauritius Mol. sugar	86.4	2.87	2.96	+0.09
19.	Superior Cebu Mats	83.2	2.00	1.93	-0.07
20.	Cuba Molasses Sugar	84.2	2.16	2.35	+0.19
21.	Taal Mats	78.5	2.57	1.97	-0.60
22.	Beet 2nd product	92.2	3.06	2.55	-0.51
23.	Java Basket ..	96.7	0.77	0.54	-0.23
24.	St. Kitts Muscovado	88.2	1.13	0.87	-0.26
25.	Syrup, Louisiana	40.9	6.80	6.13	-0.67
26.	Syrup, Sandwich Island Sugar ..	49.2	11.03	10.07	-0.96

The results obtained by the two methods differ very considerably. As the figures yielded by the Scheibler method were almost without exception lower than those found by the other process, the suspicion arose that possibly the alkali sulphates might have been partly lost by volatilisation, although this was very improbable, for the incinerations had all been carried out in a muffle exactly as prescribed.†

* From the School of Mines Quarterly, Vol. xi., No. 1.

† Zeitschrift des Vereines für Rübenzucker-Industrie, vo xvii., p. 338.

However, to settle the question, two tests were made. The sulphate ash of a Java sugar was first very carefully determined; then, in test one, there was added to a sample of the sugar equal in weight to the amount taken for the original ash determination a known amount of dried and powdered potassium sulphate; test two was carried out in exactly the same manner, only anhydrous sodium sulphate was used instead of the potassium salt. The ash determinations were then carried out as before.

The ash originally present in the sugar was 0.680. In test one, after subtracting the weight of the potassium sulphate which had been added, the ash was 0.680. In test two, after allowing for the sodium sulphate, the ash was 0.676, thus proving that the alkali sulphates did not lose in weight by the incineration.

The explanation of these differences must therefore be sought by an analysis of the ash, and the composition of the salts originally present in the sugars must be examined into.

The analyses made showed that the ashes of these sugars contain alkalies (reported in the form of potassium and sodium) ranging from 28.8 to 36.4 per cent; silica (SiO_2) was present from 1.64 to 11.08 per cent.* Two samples had less than 2 per cent; three samples had between 2 per cent and 3 per cent; two, between 3 per cent and 4 per cent; seven, between 4 per cent and 5 per cent; three, between 5 per cent and 6 per cent; three, between 6 per cent and 7 per cent; one had 8.93 per cent, and one 11.08 per cent.

The only silicates soluble in water are the silicates of the alkalies; hence one is forced to the conclusion that the alkalies in these sugars are present, at least in part, in the form of silicates. Analysis further showed the ash in most samples to be rich in sulphates, the sulphuric acid (H_2SO_4) calculated in percentage on the carbonate ash ranging from 4.17 to 31.71 per cent.

How the salts originally present in a sugar are affected by the two methods of ash determination here given is the next question to be considered. The salts in a sugar may be assumed to exist in the form of silicates, sulphates, chlorides, carbonates, phosphates, nitrates, and organic acid salts; for instance, as oxalates, tartrates, malates, and possibly as citrates.

	After simple incineration will be found as—	After incineration with sulphuric acid will be found as—
Silicates	silicates	silicates.
Sulphates	sulphates	sulphates.
Chlorides	carbonates†	sulphates.
Nitrates	carbonates	sulphates.
Carbonates	carbonates	sulphates.
Organic acid salts	carbonates	sulphates.

Looking at this table, it is evident that sugars rich in chlorides, carbonates, and organic acid salts, will, on incineration with sulphuric acid, give results that are higher than those obtained by simple carbonisation, because the molecular weight of the sulphates is greater than that of the chlorides or carbonates, into which form (*i.e.*, carbonates) the organic acid salts are transformed by simple incineration.‡ It was this fact, of course, that Scheibler bore in mind when he called for the subtraction of one-tenth from the weight of the sulphate ash; it was this fact, too, that gave rise to the difficulties of the French chemists cited, who found that Scheibler's factor would not bring the sulphate ash into agreement with the ash obtained by simple incineration.||

* This represents silica, or rather silicates in solution, as all suspended sand, &c., had been removed by filtration.

† Certainly in part, if not wholly.

‡ That the organic acid salts can be greatly in preponderance appears from analyses made by Laugier, *Comptes Rendus*, 1878, p. 27, who found in analysing the fill-mass of a refinery (fourth product), that over 70 per cent of the salts present, which themselves amounted to 10 per cent of the sugar, consisted of organic acids.

|| In France, at one time, the factor 0.8 was used in official analyses, while 0.9 was adopted in commercial work.

If, however, the sugars analysed are similar in composition to those here examined; that is to say, if they be rich in silicates and sulphates, the case is an entirely different one, for although it would be extremely difficult, if not impossible, to assign formulæ for the silicates of the alkalis (as those which occur in nature range between the limits $4M_2O, SiO_2$ and $M_2O, 2SiO_2$),* yet, as the silicates of the alkali metals "dissolve with greater facility in proportion as they contain a larger quantity of base,"† the molecular weight will, in any case, be equal to, or greater than, that of the alkaline sulphates, and, therefore, the subtraction of one-tenth will bring the figures below the true value. To illustrate this, the following table, while bringing once more the carbonate ash values previously recorded, gives the sulphate ash values as found; that is to say, *without subtraction of one-tenth*, but of course, as before, allowing for the inorganic suspended impurities.

Analysis number.	Sugar.	Polarisation.	Carbonate ash.	Sulphate ash.	Difference. The results obtained as sulphates are:—
1.	Dominica Muscovado	86.0	1.25	1.21	-0.04
2.	Java, 2nd product	86.5	1.32	1.25	-0.07
3.	"	88.8	1.06	0.90	-0.16
4.	"	86.3	1.05	0.89	-0.16
5.	"	86.7	0.81	0.68	-0.13
6.	"	87.5	1.26	1.04	-0.22
7.	Trinidad Concrete	84.0	2.47	2.32	-0.15
8.	Ilo-Ilo	86.6	1.91	1.60	-0.31
9.	"	80.8	2.30	2.20	-0.10
10.	New Orleans Muscovado	91.2	0.76	0.56	-0.20
11.	New Orleans Muscovado	80.2	3.08	2.98	-0.10
12.	New Orleans Melado	79.1	1.69	1.73	+0.04
13.	New Orleans Melado	52.0	1.42	1.23	-0.19
14.	St. Croix Muscovado	88.0	1.27	1.16	-0.11
15.	Ceroons	83.8	1.78	1.44	-0.34
16.	Brazil	84.1	1.95	1.44	-0.51
17.	Java Stroops	77.4	4.16	4.15	-0.01
18.	Mauritius Mol. Sugar	86.4	2.87	3.33	+0.46
19.	Superior Cebu Mats	83.2	2.00	2.24	+0.24
20.	Cuba Molasses Sugar	84.2	2.16	2.67	+0.51
21.	Taal Mats	78.5	2.57	2.44	-0.13
22.	Beet, 2nd product	92.2	3.06	2.85	-0.21
23.	Java Basket	96.7	0.77	0.61	-0.16
24.	St. Kitts Muscovado	88.2	1.13	0.98	-0.15
25.	Syrup, Louisiana	40.9	6.80	6.82	+0.02
26.	Syrup, Sandwich Island Sugar	49.2	11.03	11.19	+0.16

It will be seen at a glance how much better the results of the two methods agree now; but even so, the sulphate ash is, with few exceptions, *lower* than the other, and, therefore, if anything, one feels tempted to seek for a factor by which to *increase* the sulphate ash. The exceptions noted are the very ones to prove the rule, or rather to bear out the explanation given, for Nos. 26, 18, and 19 are lowest in silica, containing respectively 0.96, 1.64, and 1.69 per cent. No. 20 contains 2.64 per cent silica, but is the lowest in sulphates, and so these sugars in their composition approach more closely the beet sugars examined by the European chemists, the ash

analysis of which, made by Von Lippmann,* may be regarded as typical. In this analysis (of a carbonate ash of beet-sugar) he reports, among other constituents,—

Potassium	50.87
Sodium	9.13
Sulphuric acid	2.04
Silicic acid	0.10

In view of the important part that the ash plays in the cost and in the yield of raw sugars, it is certainly a matter of no small consideration to have an analytical method which may be depended upon.

To devise an analytical process by which the *actual amount of salts* in a sugar could be ascertained in everyday practice, that is to say, by which the salts present could be quickly and accurately determined, seems, in our present state of knowledge, an impossibility, unless, indeed, the electric-conducting power of dilute sugar solutions shall prove to be the means by which this end will be attained.†

Whether any of the numerous methods proposed for determination of the ash—as, for instance, Dubrunfaut's‡ suggestion of burning the sugars off with spongy platinum, ignition in a current of pure oxygen, or the combustion with oxide of zinc, as recently recommended by Lucien§—would prove superior to Scheibler's method, cannot here be inquired into.

The great advantage of incineration with sulphuric acid, especially as it is now practised, with addition of a little ether is not to be questioned. The possible objection as to the expense of platinum muffles, where several must be used on account of the number of daily determinations, has been overcome in our laboratory by the use of muffles made of Russian sheet-iron, which may be had at one-hundredth the cost of the platinum ware, which last, on an average, between three and four months, and which give absolutely no contamination to the sugar ashes burned off in them.

While thus fully appreciating this analytical method, there is no reason why countenance should be lent to the practice of changing an *absolute value* obtained by analysis into a *problematical figure* by means of a factor which may give results concordant, too high or too low, according to the nature of the sugar examined, and which, as far as this item is concerned, leaves to the purchaser really no clue as to how his sugars will turn out. Why not accept, as already suggested by Dubrunfaut,|| as a working factor the sulphate ash actually obtained? This, at least, represents a definite value upon which calculation may be based, and it is difficult to understand how the one-tenth subtraction can have held its sway to the present day, when its misleading influence—at least in one direction—was pointed out already ten years ago.

NOTES FROM THE LABORATORY OF SMITH COLLEGE.¶

By J. T. STODDARD.

A New Test-Tube Holder.—The annoyance experienced in using the common wooden test-tube holder led me some years ago to attempt to devise a holder which should serve its purpose more perfectly. The wooden holder is clumsy, its rubber band rots and is liable to give way at awkward moments, the peg becomes unglued and drops out, and even in its best estate it holds securely

* Zeitschrift des Vereines fur Rubenzucker-Industrie, vol. xxi., 1881, p. 399.

† Ibid., vol. xxxix., p. 432.

‡ Journal des Fabricants de Sucre, Dec. 18, 1870.

§ Bulletin de l'Association des Chimistes, 1889, p. 356.

|| Le Sucre, 1878, vol. ii.

¶ Journal of Analytical Chemistry, Vol. iv., Part 1, January, 1890.

* Watts' "Dictionary of Chemistry," vol. v. p. 244.
† Loc. cit.

only medium-sized test-tubes. Tubes of more than two centimetres cannot be inserted sideways, larger ones are not taken at all, and a separate holder must be used for small test-tubes and ignition-tubes.

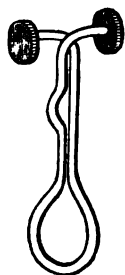
The new holder has been in use in my laboratory for four years now, and has given such good satisfaction that I venture to call attention to it in a form recently somewhat improved. It is made of brass wire, and opens by



pressure on the straight sides of the handle; its jaws open to the width of 5 c.m., and it holds firmly any tube from 5 m.m. up. It thus serves for ignition-tubes as well as for all sizes of test-tubes.

I have recently had a larger size made of stiffer wire for the purpose of holding flasks, &c. It proves very convenient as a holder of wash-bottles when one is washing with boiling-water, and also for holding beakers when decanting hot solutions. Both sizes are furnished by the Victor Manufacturing Co., Northampton, Mass.

A Modified Form of Pinchcock.—As is shown in the cut, the modification consists in making a side-bend in one of the limbs and omitting the double wire which serves as a guide in the ordinary form. The pinchcock can be opened by springing the limbs apart, and thus is



readily put on a tube connected at both ends without breaking connections; and when placed so that the tube lies in the side bend, leaves the tube open while retaining its place. The side bend was suggested by a note in *Ztschr. Anal. Chem.*, xxiv., 399.

Filtration under Pressure.—The introduction of this method of rapid filtration into my qualitative laboratory has resulted in a very considerable gain in the amount of work accomplished by the class in the time at his disposal. A quarter-inch iron pipe connects each place with a Chapman's aspirator, the pressure being regulated for the whole system by connecting at one point a side neck tube containing mercury, and having a tube open to the air thrust through the cork to a proper distance below the surface of the mercury. The use of brass gas-cocks on the exhaust pipe is not to be recommended, as they are affected by the ammonia and other gases which escape from the filtrates, and soon turn hard and often stick fast. A pinchcock on the tubing used to connect the filtering

flask is an efficient substitute, but it is better to use it only during working hours and to relieve the rubber tubing from its pressure at the close of work, plugging the tube with a short piece of glass rod. By treating the filter-papers with nitric acid of sp. gr. 1.42, as proposed by Francis (*Ztschr. Anal. Chem.*, xxvi., 351), the use of platinum cones is rendered unnecessary, and the paper is in much better condition for the removal of precipitates. In this connection I wish to call attention to the remarkable efficiency of the Chapman aspirator. I have used an inch aspirator for three or four years, in place of the ordinary air-pump, for exhausting receivers, &c., in my lectures, and find it not only gives a high vacuum (the residual pressure being that of aqueous vapour at the temperature of the water running through the aspirator), but works with great rapidity. With our water pressure of about 70 pounds, a receiver of 3600 c.c. capacity is exhausted to the above limit (at this season about 10 m.m. of mercury) in a minute and a half.

SUMMARY OF USEFUL TESTS WITH THE BLOWPIPE.*

By A. J. MOSES.

THE following selection includes only the tests used in the instruction at the Mineralogical Laboratory of the School of Mines. It is believed that the omitted tests have always been omitted for cause, either as less characteristic or less easily obtained, or from the need of some unusual or not easily handled reagent.

The details of ordinary manipulations, such as obtaining beads, flames, coatings, and sublimates, are omitted, and the results alone stated; unusual manipulations are described. The bead tests are supposed to be obtained with oxides; the other tests are, in general, true of all compounds not expressly excluded. The course to be followed in the case of interfering elements is briefly stated.†

ALUMINIUM, Al.

With Soda.—Swells and forms an infusible compound.
With Borax or S. Ph.—Clear or cloudy, never opaque.
† *With Cobalt Solution.*—Fine blue when cold.

AMMONIUM, NH₃.

In Closed Tube.—Evolution of gas with the characteristic odour. Soda or lime assists the reaction. The gas turns red litmus-paper blue and forms white clouds with HCl vapour.

ANTIMONY, Sb.

On Coal, R. F.—Volatile white coat, bluish in thin layers, continues to form after cessation of blast.

With Bismuth Flux—

On Plaster.—Orange-red coat, made orange by (NH₄)₂S.

On Coal.—Faint yellow or red coat.

In Open Tube.—Dense, white, non-volatile, amorphous sublimate. The sulphide, too rapidly heated, will yield spots of red.

In Closed Tube.—The oxide will yield a white fusible sublimate of needle crystals, the sulphide a black sublimate red when cold.

Flame.—Pale yellow-green.

With S. Ph.—Dissolved by O. F. and treated on coal with tin in R. F. becomes grey to black.

Interfering Elements.

Arsenic.—Remove by gentle O. F. on coal.

* From the *School of Mines Quarterly*, vol. xi., No. 1.

† *School of Mines Quarterly*, vol. viii., p. 259, and vol. x., p. 321.

‡ Certain phosphates, borates, and fusible silicates become blue in absence of alumina.

§ This coat may be further tested by S. Ph. or flame.

Arsenic with Sulphur.—Remove by gently heating in closed tube.

Copper.—The S. Ph. bead with tin in R. F. may be momentarily red, but will blacken.

Lead or Bismuth.—Retard formation of their coats by intermittent blast, or by boracic acid. Confirm coat by flame, not by S. Ph.

ARSENIC, As.

On Smoked Plaster.—White coat of octahedral crystals.

On Coal.—Very volatile white coat and strong garlic odour. The oxide and sulphide should be mixed with soda.

With Bismuth Flux.

On Plaster.—Reddish orange coat, made yellow by $(\text{NH}_4)_2\text{S}$.

On Coal.—Faint yellow coat.

In Open Tube.—White sublimate of octahedral crystals. Too high heat may form brown suboxide or red or yellow sulphide.

In Closed Tube.—May obtain white oxide, yellow or red sulphide, or black mirror of metal.

Flame.—Pale azure blue.

Interfering Elements.

Antimony.—Heat in closed tube with soda and charcoal, treat resulting mirror in O. F. for odour.

Cobalt or Nickel.—Fuse in O. F. with lead and recognise by odour.

Sulphur.—(a). Red to yellow sublimate of sulphide of arsenic in closed tube. (b). Odour when fused with soda on coal.

BARIUM, Ba.

On Coal with Soda.—Fuses and sinks into the coal.

Flame.—Yellowish green improved by moistening with HCl.

With Borax or S. Ph.—Clear and colourless, can be framed opaque-white.

BISMUTH, Bi.

On Coal.—In either, flame is reduced to brittle metal and yields a volatile coat, dark orange-yellow hot, lemon-yellow cold, with yellowish white border.

With Bismuth Flux.*

On Plaster.—Bright scarlet coat surrounded by chocolate-brown, with sometimes a reddish border. The brown may be made red by ammonia.†

On Coal.—Bright red coat with sometimes an inner fringe of yellow.

With S. Ph.—Dissolved by O. F. and treated on coal with tin in R. F. is colourless hot, but blackish grey and opaque cold.

Interfering Elements.

Antimony.—Treat on coal with boracic acid, and treat the resulting slag on plaster with bismuth flux.

Lead.—Dissolve coat in S. Ph. as above.

BORON, B.

All borates intumesce and fuse to a bead.

Flame.—Yellowish green. May be assisted by—(a) Moistening with H_2SO_4 ; (b) Mixing to paste with water and boracic acid flux ($\frac{4}{5}$ pts. KHSO_4 , 1 pt. CaF_2); (c) By mixing to paste with H_2SO_4 and NH_4F .

BROMINE, Br.

With S. Ph. Saturated with CuO .—Treated at tip of blue flame, the bead will be surrounded by greenish blue flame.

In Matrass with KHSO_4 .—Brown choking vapour.

Interfering Elements.

Silver.—The bromide melts in KHSO_4 and forms a

* Sulphur two parts, potassic iodide one part, potassic bisulphate one part.

† May be obtained by heating S. Ph. on the assay.

blood-red globule which cools yellow and becomes green in the sunlight.

CADMIUM, Cd.

On Coal R. F.—Dark brown coat, greenish yellow in thin layers. Beyond the coat, at first part of operation, the coal shows a variegated tarnish.

On Smoked Plaster with Bismuth Flux.—White coat made orange by $(\text{NH}_4)_2\text{S}$.

With Borax or S. Ph.—O. F. clear yellow hot, colourless cold, can be flamed milk-white. The hot bead touched to $\text{Na}_2\text{S}_2\text{O}_3$ becomes yellow.

R. F. becomes slowly colourless.

Interfering Elements.

Lead, Bismuth, Zinc.—Collect the coat, mix with charcoal dust, and heat gently in a closed tube. Cadmium will yield either a reddish brown ring or a metallic mirror. Before collecting coat, treat it with O. F. to remove arsenic.

CALCIUM, Ca.

On Coal with Soda.—Insoluble and not absorbed by the coal.

Flame.—Yellowish red improved by moistening with HCl.

With Borax or S. Ph.—Clear and colourless, can be flamed opaque.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.

Annual Meeting, May 1, 1890.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1889, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £82,000, entirely derived from the contributions and donations of the Members.

Fifty-one new Members were elected in 1889.

Sixty-three Lectures and Nineteen Evening Discourses were delivered in 1889.

The books and pamphlets presented in 1889 amounted to about 283 volumes, making, with 539 volumes (including periodicals bound) purchased by the Managers, a total of 822 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as officers for the ensuing year:—

President—The Duke of Northumberland, K.G., D.C.L., LL.D.

Treasurer—Sir James Crichton Browne, M.D., LL.D., F.R.S.

Secretary—Sir Frederick Bramwell, Bart., D.C.L., F.R.S., M.Inst.C.E.

Managers—Sir Frederick Abel, C.B., D.C.L., F.R.S.; Sir Benjamin Baker, K.C.M.G., M.Inst.C.E.; The Right Hon. Arthur J. Balfour, M.P., LL.D., F.R.S.; George Berkeley, M.Inst.C.E.; William Crookes, F.R.S.; Warren W. de la Rue; Edward Frankland, D.C.L., LL.D., F.R.S.; Charles Hawksley, M.Inst.C.E.; William Huggins, D.C.L., LL.D., F.R.S.; David Edward Hughes, F.R.S.; Alfred Bray Kempe, M.A., F.R.S.; The Right Hon. Earl Percy; Edward Pollock; William Chandler Roberts-Austen, F.R.S.; Basil Woodd Smith, F.R.A.S.

Visitors—John Wolfe Barry, M.Inst.C.E.; Shelford

Bidwell, M.A., F.R.S.; Alfred Carpmal; Arthur Herbert Church, M.A., F.R.S.; Ernest H. Goold, F.Z.S.; George Herbert; John Hopkinson, M.A., F.R.S., M.Inst.C.E.; John W. Miers; Sir Thomas Pycroft, M.A., K.C.S.I.; Lachlan Mackintosh Rate, M.A.; Sir Owen Roberts, M.A., F.S.A.; Arthur William Rücker, M.A., F.R.S.; John Bell Sedgwick, J.P., F.R.G.S.; Joseph Wilson Swan; Thomas Edward Thorpe, Ph.D., F.R.S.

General Monthly Meeting, May 5, 1890.

His Grace the DUKE OF NORTHUMBERLAND, K.G.,
D.C.L., LL.D., in the Chair first;
afterwards,

SIR JAMES CRICHTON BROWNE, M.D., LL.D., F.R.S.

The following Vice-Presidents for the ensuing year were announced:—

Sir Frederick Abel, C.B., D.C.L., F.R.S.; William Crookes, F.R.S.; Edward Frankland, D.C.L., LL.D., F.R.S.; William Huggins, D.C.L., LL.D., F.R.S.; The Right Hon. Earl Percy; Basil Woodd Smith, F.R.A.S., F.S.A.; Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer; Sir Frederick Bramwell, Bart., D.C.L., F.R.S., Hon. Secretary.

Harry Baldwin, M.R.C.S., A. R. Binnie, M.Inst.C.E.; Miss Frances Busk, J. S. Jeans, A. Kirkman Loyd, Ronald A. Scott, F.R.G.S., F.Z.S.; Mrs. John I. Thorneycroft, John Jewell Vezey, F.R.M.S., and Laundry Walters, were elected Members of the Royal Institution.

John Tyndall, D.C.L., LL.D., F.R.S., was elected Honorary Professor of Natural Philosophy.

The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S., was elected Professor of Natural Philosophy.

NOTICES OF BOOKS.

The Art of Paper-Making. A Practical Handbook of the Manufacture of Paper from Rags, Esparto, Straw, and other Fibrous Materials, including the Manufacture of Pulp from Wood-Fibre, to which are added Details of Processes for recovering Soda from Waste Liquors. By ALEXANDER WATT. London: Crosby Lockwood and Son.

MR. WATT may almost be pronounced the "Admirable Crichton" of chemical technology. He has already produced works on such very distinct subjects as soap-making, the leather manufacture, electro-metallurgy, and the art of electro-deposition. These treatises are not mere compilations, but practical works, evincing an actual acquaintance with the arts in question. That they have met recognised wants appears at once from the fact that all of them have appeared in several successive editions. We believe that the volume now before us will also prove useful and acceptable.

The author first speaks of cellulose, its behaviour with acids, its physical and microscopic properties, its determination, and the recognition of its chief modifications. He next comes to the multifarious materials used in the paper manufacture, whereby we are happy to find that he does not overlook the importance of the thorough disinfection of rags. These residues of human life and activity are especially dangerous if imported, as it often happens, from countries where a large part of the population live in a chronic state of misery and degradation, and where personal dirtiness extends to all classes. Few more effective vehicles of zymotic disease can be conceived than rags of such kinds. It must not be supposed that the prevalence of cholera or yellow fever is the only occasion for unusual vigilance. Nor is the danger greatest in rags introduced from India, Egypt, or Spain. Consignments from Russia must require even more scrupulous

care. Mr. Watt figures and describes a "disinfecting machine," by which suspected material may be treated in the bale without the expense, delay, and risk of opening out the packages.

In a chapter on the treatment of rags we find the remark that woollen rags are only used to a very moderate extent "in blotting and filtering-papers, and also in coarse papers and wrappers." For filter-papers woollen rags are, we submit, a most unsuitable material. Such papers require to be rapidly and completely combustible—a property with which the presence of wool-fibre would greatly interfere. It may here be remarked that Mr. Watt gives no instructions for the manufacture of filter-paper—a branch of the trade in which England has never taken as high a standing as Sweden, and, of late years, as Germany.

The processes for the treatment of esparto and of wood are very fully described. There is no mention of the prolonged litigation which has arisen in the German courts concerning the Mitscherlich process. Our author, however, seems to object to the acid methods of reducing wood to a pulp. The mechanical processes he recognises produce an inferior article. One of the defects of papers into which mechanical wood-pulp enters largely is that they are very readily discoloured, not only by the sun's rays, but even by the electric light. This fact has actually been utilised by a partisan of gas-lighting as an argument against the electric light.

Among methods for bleaching paper we find mention of certain electrolytic processes, which, whether they are legally valid or not, present a strong family likeness to the device for which the author's brother, Mr. Charles Watt, obtained a patent on September 25, 1881.

We do not find that the author throws out any cautions as to the escape of waste bleach-liquors into streams. Against this nuisance all authorities on the pollution of rivers and on sewage disposal have protested as destructive to fish and as unfitting the water alike for industrial and for domestic uses.

There is a favourable mention of the improved process of Dr. Lunge, who liberates chlorine or hypochlorous acid from the bleaching lime by the addition, not of the sulphuric or hydrochloric acid, but of the acetic—a very happy invention.

The "loading" materials in vogue are duly noticed, kaolin and calcium sulphate. It is certainly interesting to observe under what varying guises these two minerals figure, haunting us as they do in our dining-rooms, our dressing-rooms, and even in our studies. A better ingredient for loading is agalite, a species of asbestos which has a fibrous texture. It must be admitted that in all but the highest classes of paper "loading," if kept in moderation and skilfully applied, has its advantages. It gives the paper a smoother surface, into which the point of pen or pencil is less disposed to sink.

In speaking of colouring paper stock the author forgets that not all the aniline colours are liable to be injuriously affected by the acid of the alum used in sizing.

The "super-calendered" paper, now so much in fashion that we have heard the failure of a journal ascribed to its being printed on paper with a matt surface, is open to a very serious objection. By the strong reflection of light it injures the eyes of persons who have to read much.

Space, or the want of it, does not permit us to prolong our examination of this interesting work. But we can do no other than recommend it to all of our readers who are connected with or interested in the paper trade, as well as to technological students.

The Extension of Public Analysis. By CHARLES E. CASSAL, Public Analyst for St. George's, Hanover Square, Kensington, Battersea, and High Wycombe.

THIS paper was read at the Worcester Congress of the Sanitary Institute, where it may be said to have figured

as a redeeming feature. The author contends for two much-needed reforms, the adequate enforcement of the existing law and an extension of public analysis. Both these tasks are difficult. The former point is prevented by the blindness of a large part of the magistracy, stipendiary as well as unpaid. They cannot see that the adulterator stands morally on the same plane as the pick-pocket or the shop-lifter, and hence they dismiss fully proved cases, or at best inflict fines which are perfectly farcical. As for the extension of the law, the case is still worse. Any bill having this object would be thrust aside by the necessities of faction, and any ministry which should adopt it would have, at the next election, to encounter the "solid vote" of all those classes of traders whose tricks were interfered with. We quite agree with Mr. Cassal that the analysis of gas and of water should be placed in the hands of competent chemists. Medical officers of health are not always fit to conduct analytical work, and their duties should be kept quite distinct from those of the public analyst. The notion of appointing military men as inspectors of public water supply is regarded on the Continent as farcical. John Bull, it is contemptuously said, "puts his army and navy in the hands of civilians and, as compensation, entrusts matters of public health and of higher education to military officers."

The author most justly urges that poisonous quackeries, hair-dyes, soaps, cosmetics, dyes, wall-papers, children's toys, &c., should be liable to seizure and examination. If poisons are discovered where their presence is unsafe or unessential the punishment ought to be signal.

The tabular list of articles examined and found adulterated shows how much work remains to be done. Perhaps the worst figure is made by Nottinghamshire, where, out of 120 samples taken in 1887, 49, or 40·8 per cent, were found adulterated.

Mr. Cassal may rest assured of our sympathies and support in his endeavours to arouse the authorities and the legislature to a sense of their duty.

Proceedings of the American Pharmaceutical Association at the Thirty-seventh Annual Meeting, held at San Francisco, June, 1889; also, the Constitution, By-Laws, and Roll of Members. Philadelphia: The Association.

THE portion of this report in which we feel interested is that comprising the scientific papers laid before the meeting. The burning question of arsenic in wall-papers returns again. Mr. D. H. Galloway, the author of the paper, declares that when he began his inquiry he supposed that it could be decided by the mere appearance of a paper whether it is arseniferous. This, however, he found is not the case; arsenic is not confined to green colours, but is met with in reds and browns, where it is hard to conjecture what the necessity or even the pretext for its use may be. Prof. Wood, in the Report of the Massachusetts Board of Health for 1883, specifies the following articles as occasionally arseniferous:—"Dress goods, muslins, linen, artificial flowers, curtains, gloves, boot-linings, paper collars, linen collars (one collar containing 10·4 grs. (doubtless grains) of As_2O_3), hat-linings, coloured stockings, linings in baby carriages, bed hangings, coloured candles, and confectionery." To this list may be added painted toys, and even so-called French chalk. Some years ago a woman in one of our northern towns bought some prepared chalk as a cure for heart-burn, and was, by mistake, served with French chalk; she died shortly after with the usual symptoms of arsenical poisoning, and the chalk was found on analysis to contain about 25 per cent of As_2O_3 . Query, the motive?

In the paper before us it is further stated that "jellies are made out of glucose (?), and are largely coloured with aniline colours. You will find by testing these jellies that arsenic is present, whether in large quantities or not I do not know, but I know they are contaminated by

aniline colours, which contain arsenic." We must here declare, as the result of our own experience, that the aniline colours now sold by the most eminent manufacturers are free from arsenic.

An illustrated paper on photo-micrography is well worthy of notice. The composition of glucose, as met with in trade, is said to be 40—50 per cent of (fadtious) grape-sugar and the same quantity of dextrin. We may here ask whether this glucose is not one of the channels through which arsenic is conveyed into articles of food and drink? The sulphuric acid employed in the manufacture of glucose is not always perfectly free from arsenic.

It is satisfactory to learn that a firm who attempted to sophisticate refined cane-sugar with glucose lost half a million dollars by the experiment.

The chapter on patent and trade-mark laws is very valuable. We must, however, protest against a quotation from the "Encyclopædia Britannica" on the subject of copyright. The author says:—"Historically and in legal definition there would appear to be no doubt that copyright, as regulated by Statute, is a monopoly." In reply, we say that, according to Blackstone, a monopoly is a privilege by which the public at large are prevented from doing something which they were previously free to do. But it is obvious that no one is free to publish a book before it is written, so that the public is deprived of nothing. The sophistry of C. Renouard, here quoted, would be fatal not merely to property in literary works and inventions, but to property of all kinds.

The so-called "patent medicine" business, now worked not so much under the patent laws as under the Copyright and Trade Marks Act, is strongly and justly denounced. The method used in America, which differs little from that pursued in England, is thus described:—"A new preparation is devised, or a compound of old and well-known drugs is mixed, and a name invented by which to designate the compound. This name is registered as a trade-mark; the true or working formula of the preparation is kept secret, and the preparation is marketed under the alleged protection of the trade-mark law. By this system knowledge is concealed, progress in science and art hindered, error inculcated, and the public injured instead of being benefitted." An utterance of this kind from the United States is all the more welcome, as that country is now inundating the world with quack nostrums.

New York State Board of Health. Report of WILLIS G. TUCKER, M.D., Ph.D., Analyst of Drugs.

THIS report refers to the official inspection and analysis of drugs. The classification in use is "good quality" when the preparations fulfil the requirements of the United States Pharmacopœia; "fair" if neither intentionally sophisticated nor decidedly below the standard; and "inferior" if evidently falsified, deficient in strength, partially decomposed, &c. It is remarked that the samples bear no direct relation to their quality. Out of 505 samples examined 43·8 per cent were reported as good, 17·4 as fair, 26·0 as inferior, 11·6 "not as called for," and excessively strong 1·2 per cent. Some of the articles reported "not as called for," were safflower, sold in place of saffron! Saffron has possibly certain medicinal uses, but as a dye-ware it is little better than rubbish.

There is a special report on cigarettes which had been said to be adulterated with opium. This did not prove to be the case, and from financial reasons is very improvable. Dr. Tucker, however, complains of the common sale and use of cigarettes by young children, "whose morals are depraved by the suggestive and openly indecent pictures used to advertise certain brands, which pictures are freely exposed in the store windows, and packed in the boxes with the cigarettes."

Another special report relates to vermin killers, which

may be dangerous to human life, and concerning which the Assembly of the State of New York and the State Board of Health seem greatly exercised.

Poisons for rats may be rendered perfectly safe if made up in the form of *candles*, arsenical, phosphorised, or containing strychnine. Neither children nor domestic animals will eat such dainties. The outcry against the free sale of poisons on either side of the Atlantic seems to be inconsistent, even to the verge of hypocrisy, so long as no restrictions are placed on the traffic in fire-arms and ammunition. The legitimate uses of poisons are far more numerous than those of revolvers and cartridges, and the evil which they can occasion even in bad or careless hands is much slighter.

CORRESPONDENCE.

SCIENTIFIC TERMINOLOGY.

To the Editor of the *Chemical News*.

SIR,—It is truly said that when a word has once been dirtied no human power can cleanse it. At present, a termination of frequent use in organic chemistry, and a set of paronyms which occur in all scientific and philosophical writings, have been so misused by outsiders that they should, I submit, if possible, be abandoned.

The termination in question is *ine*. We find the inventors of so-called "proprietary" medicines, &c., using it as a tail-piece to the names of their nostrums, though these are mere mixtures, not chemical individuals—not to speak of alkaloids. Not long since I saw a disinfectant advertised as "Listerine"!

Would it not be well to dispense with this termination in chemical treatises? The halogens might be simply called fluor, chlore, brome, and iode; whilst the alkaloids might resume the termination *a* or *ia*, which was at one time in very general use.

A still worse case is the abuse of the term "phenomenon." Every scientific man is, of course, agreed as to the legitimate and etymological meaning of the word—which, for once, coincide. But, unfortunately, showmen and strolling actors applied it to something marvellous. Their example has been followed to such a degree that even eminent physicians are not ashamed to speak of "phenomenal agents." It would be easy in chemical and physical writings to use such words as "appearances," "manifestations," "results," or "reactions" in place of "phenomena."—I am, &c.,

J. W. SLATER.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 16, April 21, 1890.

Obituary.—At the session of April 21 the president announced the death of Prof. Peligot, which took place on Tuesday, April 13. We hope to lay before our readers a sketch of his prolonged scientific activity.

Formation-heat and the Reactions of Hydroxylamine.—MM. Berthelot and André.—The authors give the formation-heat of this compound as 23.8 cal.

Preparation of Iridium Dioxide.—G. Geisenheimer.—The author prepares the hydrated dioxide by heating 3 grms. of iridium to redness for two or three hours in a golden crucible with 10 grms. caustic soda and 3 grms.

sodium nitrate. The mass, when cold, is taken up with boiling water.

Action of Hydrogen Peroxide upon the Oxy-compounds of Manganese.—A. Gorgen.—Contrary to the usual opinion the author finds that in contact with pure crystalline anhydrous dioxide the oxygenated water splits up instantly, but requires about an hour; the effect upon the dioxide varies according as the oxygenated water is slightly alkaline or more or less acid. In experiments where hydrated manganous oxide was put in contact with an excess of oxygenated water the degree of oxidation reached exceeds that of Mn_2O_3 .

Preparation and Formation-Heat of Sodium Erythrate.—M. de Forcrand.—From analogy this heat may be estimated as between 215 and 220 cal.

Chlorine Derivatives of the Amylamines.—A. Berg.—An account of monochloramylamine, dichloramylamine and chlorodiamylamine.

The Alcoholic Fermentation of Invert-Sugar.—U. Gayon and E. Dubourg.—It results from the author's researches that the alcoholic ferments differ not merely by their form, their action upon saccharose, their fermentive power, &c., but also by their mode of action upon the constituent elements of invert-sugar.

Alcoholic Fermentation and the Transformation of Alcohol into Aldehyd by the Fungus of the Lily of the Valley.—Georges Linossier and Gabriel Roux.—The alcoholic fermentation set up by the fungus in question has rather the characters of fermentation occasioned by mucus than those of fermentation by beer-yeast. Hence we are justified in eliminating the fungus of the lily of the valley from the group of *Saccharomyces*.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6

Examination of Resins.—Kremel.—The author gives the acid—the Köttsdorf—and the iodine numbers of the most important resins. The potassa taken up by boiling the sample for half an hour with semi-normal alcoholic potassa-lye and titrating back the excess with semi-normal hydrochloric acid and phenolphthalein, is given in a table by R. Williams, taken from the *CHEMICAL NEWS*. The numbers, multiplied by 10, correspond to the Köttsdorf figures.

Approximate Determination of Resin in Ceresine.—H. Symons.—From the *Pharm. Journal*.

Two New Analytical Methods for the Valuation of Manganese Peroxide.—Paul Charpentier.—Already noticed under *Comptes Rendus*.

Two Impurities in Litharge.—Th. Salzer (*Pharm. Central Halle*).—The impurities are nitrous acid and gypsum. The nitrous acid is dissolved on treating the sample with water. It dissolves also in the preparation of basic lead acetate. Gypsum in litharge renders water strongly alkaline, and may be removed by continued washing.

Valuation of Roofing Slate.—H. Brunner.—The absence of calcium carbonate, tesseral crystals of pyrites, and orthorhombic crystals of markasite must be ascertained microscopically. The height to which water will rise in slips of the sample must also be determined.

Quantitative Determination of Some Tar Colours; in particular, Naphthol Yellow S, Picric Acid, and Certain Azo-Colours.—Christopher Rawson and E. Knecht (*Chemiker Zeitung*).—The authors dissolve 10 grms. "night blue" in 50 c.c. glacial acetic acid and dilute to 1 litre. Solutions of the colours in question are then made of 1 grm. per litre. The *modus operandi* is as follows:—10 c.c. of the blue solution is measured with a pipette into a flask and a known quantity of the picric or naphthol-yellow solution is added. After about a minute the liquid is filtered and the colour of the filtrate

examined. The experiment is then repeated with a fresh quantity of the blue solution and more or less of the picric acid or naphthol yellow solution is added. The mixture is again filtered, the colour of the filtrate examined, and the experiment is repeated until the next drop of the yellow solution produces a yellow colouration in the filtrate. The reaction is applicable to the examination of "night blue" and crystal violet.

Quantitative Determination of Wood-Stuff in Paper.—R. Godefroy and M. Coulon (*Gewerbe Museum Wien*).—Cellulose which has been extracted by boiling with water, alcohol, and ether does not reduce dilute solution of gold chloride at a boil, whilst wood-paste has a powerful reductive action. In examining papers the sample, carefully weighed, is treated first with cold and then with boiling water to remove size, and the alumina present is then extracted by treatment with a boiling solution of tartaric acid in alcohol at 80 per cent. It is dried, extracted with alcohol and ether, and then treated with gold chloride.

Microscopic Examination of Cattle-Foods.—Th. Ritter v. Weinzerl.—100 grms. of the sample, which must have been carefully mixed up, are separated into four portions by passing through sieves with meshes of 1.5, 1, 0.5, and 0.25 m.m. in size. The nature of the foreign ingredients is next ascertained by examination, first with a lens of low power and then with the microscope. The weight of the four portions is then ascertained, and in particular millet-flour and fragments of millet husks are separated optically.

Determination of Chlorine in the Ash of Plants.—Ad. Jolles (*Zeitschrift für Nahrungsmittel*) carbonises 10 grms. of the sample at a low temperature, grinds up the carbon, and moistens it with an alcoholic solution of sodium carbonate (the strength of the alcohol and the proportion of the salt are not given). The alcohol is then burnt off, the carbon pulverised again, soaked again as before, and burnt off twice or thrice, and finally incinerated at dull redness. About 0.5 gm. of the ash is perfectly extracted with cold water containing nitric acid, the silica is separated, though in what manner the author does not mention, the filtrate is run into a quarter litre flask and filled up to the mark. 25 c.c. of this liquid are then accurately neutralised and the chlorine is determined by titration.

Valuation of Coca Leaves.—H. J. Pfeifer.

Valuation of Crude Cocaine from Peru.—E. R. Squibb.—Both these papers are taken from the *Chemiker Zeitung*, to which the reader is referred (vol. xi., p. 818; and xiii., p. 342).

Determination of Ethereal Oils and Essences.—Alb. Levallois.—Noticed under *Comptes Rendus* (vol. xcix., p. 917).

Spectroscopic Behaviour of Ethereal Oils.—W. A. Tichomirov (*Pharm. Zeit. für Russland*).—If fresh colourless oil of citron flowers is shaken up with a saturated watery solution of acid sodium sulphite, after separation of the layers the upper stratum appears first orange, then red, and lastly purple. If the oil thus coloured is diluted until the part of the absorption spectrum between 9 and 10 of the scale is no longer darkened a characteristic absorption-spectrum is obtained. The author appears to have used the spectroscope of Schmidt and Haensch.

Examination of Official Grey Mercurial Ointment.—E. Dietrich.—For this paper we must refer to the original.

A New Reaction of Phenacetine.—E. Ritsut (*Pharm. Zeitung*).—If phenacetine is dissolved in cold strong sulphuric acid and there are added a few drops of strong nitric acid the solution at once turns yellow. If more nitric acid is added a colouring-matter of a pure citron yellow separates out.

Examination of Potassium Iodide for Nitrate.—O. Schwarz (*Pharm. Zeitung*).—0.5 gm. of the sample, 1 gm. ground copper sulphate, and 0.8 gm. ground sodium sulphite are placed in a test-tube and covered with 10 c.c. water. The mixture is heated over the naked flame until all the iodine has been separated out as white copper iodide, and the supernatant liquid has a bluish colour. In the filtrate, nitric acid, if present, may be detected by the ordinary reagents.

Determination of Urea.—L. Bleibtren (*Pfluger's Archiv*).—finds that his method, which depends on the splitting up of urea by means of phosphoric acid at high temperatures, is applicable to the urine of dogs.

The Determination of Urea by Alkaline Hypobromites.—R. Luther (*Zeitsch. Physiol. Chemie*) shows that the cause why this process does not yield the total nitrogen is that about 1½ per cent of the nitrogen, after the evolution of gas has ceased, remains in a form in which it can be obtained by distillation with alkali as ammonia. Another portion (3–4 per cent) is oxidised to nitric acid.

Determination of Uric Acid in Human Urine.—W. Camerer (*Zeit. f. Biologie*).—The uric acid is precipitated with ammoniacal solution of silver, and the uric acid is calculated from the nitrogen in the precipitate.

Rapid Determination of Iron in Blood.—L. Lapique (*Soc. Biologique*).—Two grms. blood are heated with 3 c.c. pure sulphuric acid in a flask placed in a slanting position until the coagulum first formed is redissolved. It is then let cool and heated again after the addition of a few drops of pure nitric acid until a clear, slightly coloured liquid is obtained which no longer turns brown on heating. It is then diluted and boiled for a few minutes. When cold it is diluted to 40 c.c., and 10 c.c. of a 20 per cent solution of ammonium sulphocyanide are added. The iron is then determined colorimetrically.

Detection of Traces of Mercury in Animal Liquids.—E. Brugnati (*Riforme Medica*).—The author utilises the power of mercurial vapours to reduce gold. 50–100 c.c. of the liquid are acidified with a few drops of hydrochloric acid on the water-bath along with copper wire or copper powder which has previously been ignited in a current of hydrogen, heated to 50°–60°, and then shaken for five minutes. The copper is washed with water and placed in a glass capsule along with an ignited fragment of porcelain which has been moistened with a drop of a 1 per cent solution of gold chloride. The capsule is covered with a watch-glass and heated on the water-bath, when red or violet spots with a gold reflection appear on the porcelain.

Quantitative Determination of Mercury in Urine.—R. Winternitz (*Archiv für Pathologie*).—This paper requires the two accompanying illustrations.

Detection and Estimation of Sugar in Urine.—L. Crismes (*Annal. de la Soc. Med. de Liege*).—The author's process turns on the conversion of saffranine into colourless products by reduction.

Detection of Albumen in Urine.—A. R. Cohen (*Weekblad Nederl. Tijd. voor Geneesk.*).—The reagents employed are a solution of bismuth iodide in potassium iodide and a Lugol's solution prepared with acetic acid.

Detection of Blood and Pus in Urine.—C. v. Brücke.—The author adds to 5–6 c.c. urine, 1 c.c. oil of turpentine, and 1 c.c. tincture of guaiacum. A blue colour shows the presence of blood.

Detection of Melanine and Melanogen in Urine.—R. v. Jaksch (*Zeit. Phys. Chemie*) adds moderately diluted solution of ferric chloride, which gives a black precipitate.

An Improvement in the Marsh Apparatus.—E. Lehmann.—The pieces of zinc serving for generating the gas are fixed to a glass rod which works air-tight in the stopper and can slide.

New Method for the Microscopic Examination of Paper.—F. v. Höhnelt (*Gewerbe Museum Wien per Chemiker Zeitung*).—The author separates paper fibres into three groups:—(1) Old rag fibre (linen, hemp, cotton); (2) the superior substitutes, consisting chiefly of cellulose (wood-cellulose, straw-cellulose, esparto fibre); (3) the inferior substitutes, woody fibre and jute; by means of the colours produced with iodine and sulphuric acid. He omits to give the sp. gr. of the sulphuric acid, which, he says, is quite essential. He takes linen and cotton fibres from white rags, also some wood-cellulose and white straw-stuff, and boils the fibres together for a few minutes in potassa-lye at 1 to 5 per cent. He washes the lye away and places very small quantities of each kind on the object bearer. It is important that the fibres do not form knots or lumps, but must be carefully teased out with the needle. After the water has been removed by twice pressing in filter-paper he adds a drop of solution of iodide in potassium iodide, so strong that a drop 3 c.m. thick, though clear and transparent, must appear ruby red. The drop must entirely cover the fibres. After one minute's or two minutes' contact the moisture is completely removed by pressure with filter-paper and the fibres are moistened with a drop of sulphuric acid and the cover-glass is applied. Cotton, flax, and hemp must appear of a fine violet-red; wood- and ordinary straw-cellulose pure blue or grey-blue. By this procedure, applied to paper, cotton, hemp, flax, jute bleached white, China-grass and paper-mulberry appear violet-red, wood- and common straw-cellulose appear pure blue, wood-stuff and unbleached jute dark yellow. If the papers contain esparto or maize fibres the sulphuric acid must be more concentrated. The process is applicable only to fine papers.

Examination of Essential Oils.—H. Hager (*Pharm. Central-Halle*).—The author utilises their behaviour with a mixture of equal parts by weight of glycerin (sp. gr. 1.259—1.262) and absolute alcohol. In this manner the oils are divided into two groups, the one forming a turbid solution with two volumes of the alcoholic glycerin and the other a clear solution. Of the former class some remain turbid, even with 16 vols. of the reagent, whilst others become clear if mixed with 3, 4, 5, &c. vols.

MEETINGS FOR THE WEEK.

- MONDAY, 12th.**—Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
- TUESDAY, 13th.**—Royal Institution, 3. "The Art of Engraving—1. Wood Engraving," by Louis Fagan.
— Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
— Society of Arts, 8. "The Use of Alloys in Art Metal Work," by Prof. W. C. Roberts-Austen, F.R.S.
- WEDNESDAY, 14th.**—Society of Arts, 8. "Prof. Elihu Thomson's Electro-Magnetic Induction Experiments," by Dr. J. A. Fleming, M.A.
— Geological, 8.
— Microscopical, 8.
- THURSDAY, 15th.**—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
— Society of Arts, 5. "Jamaica and its Forthcoming Exhibition," by C. Washington Eves, C.M.G.
— Society of Arts, 8. "Design Applied to Wood-carving," by Lewis F. Day.
— Chemical, 8. Ballot for the Election of Fellows. "On Diethylphosphorous Acid," by Professor Thorpe, F.R.S., and Barker North. "The Ten Isomeric Dichloronaphthalenes" and "The Action of Chlorine on Naphthalene and Naphthalene Derivatives," by Prof. Armstrong and W. P. Wynne. "A Third Naphthaquinone," by Prof. Meldola and Frank Hughes.
— Institute of Electrical Engineers, 8.
- FRIDAY, 16th.**—Royal Institution, 9. "The Photographic Image," by Prof. Raphael Meldola, F.R.S.
— Physical, 5. "On Huyghens' Gearing in Illustration of Electric Induction," by Lord Rayleigh. "Dr. R. König's Researches on the Physical Basis of Music," by Prof. S. P. Thompson.
- SATURDAY, 17th.**—Royal Institution, 3. "Recent Excavations in Greece," by Dr. Charles Waldstein.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1590.

ON THE MAGNETISATION OF METALS.

By THOMAS T. P. BRUCE WARREN.

It is well known that if a bar of iron or steel be magnetised, there is a linear increase in the magnetic "line of direction," but I am not aware of any previously published experimental data showing whether the increment is cubical, or whether the extension in length, or "line of direction," is accompanied with a diminution in the other linear directions of the mass. My experiments, which have been frequently repeated, show that there must be a diminution in the transverse section of a rod, for the same rod, when magnetised, occupies the same bulk as before being magnetised; in fact, there seems to be a slight diminution. I hope to deal more fully with this portion of the subject in a future communication.

I cannot find that any experiments have been made showing the effects of cubical compression if, for instance, a bar of iron or steel be rigidly prevented from altering its dimensions, would it be possible for the same to acquire a high degree of magnetisation relatively, when under no restraint? The solution of this problem might throw much light on the behaviour of the dipping needle when traversing a country where magnetic rocks are supposed to exist.

Bearing upon this, we must not omit to take into account the screening effect due to the magnetic permeability of the various geological deposits overlying a stratum of high magnetic susceptibility.

An arrangement which I designed some time ago, and which I termed a "Torpedo-finder," is based upon these facts. The position of a submerged torpedo, anchor, or any piece of iron may be indicated by means of the magnet, but, unfortunately, the low permeability of water involves the lowering of the magnet to within a short depth of the plane containing the submerged mass.

An electro-magnet, or solenoid, may be made magnetically stronger than an ordinary magnet. The electro-magnet is lowered to within a few feet of the bottom, the depth of which has been previously ascertained by careful sounding. The electro-magnet is excited by a primary or secondary battery. By means of a delicate dynamometer, the strain due to the electro-magnet and its leading wires are noted, the battery power is increased, when any increased pull will indicate the existence of some disturbing cause in the neighbourhood; by keeping the magnet clear of the bottom and gently steering we avoid uncertainty in the dynamometer indication, as is experienced in dragging over a rough or uneven bottom.

ESTIMATION OF AMMONIA BY RUFFLE'S METHOD.

By ALEXANDER BUCHAN, F.I.C.

AN objection to this method, particularly to those who use iron tubes, is the fusing of the contents of the tube and the consequent trouble of cleaning; so much so, that Mr. Ruffe (*Journal of the Chemical Society*, March, 1881) gives very full directions as to how this can best be done.

If, instead of exactly following the modification of the Association of Official Agricultural Chemists (*CHEMICAL NEWS*, vol. lv., p. 6), one uses soda-lime prepared as follows, instead of ordinary soda-lime, the mixture does not fuse and there is no trouble in cleaning out the tubes:—

Grind quicklime and washing-soda through a riddle of sixteen holes to the lineal inch, mix in equal proportions, and heat over an ordinary fire, in an iron pot, stirring all the time, until no more watery vapour is given off; the pot should only be one-third full, as the mixture swells very much.

The author has tried many plans for the conjoint estimation of nitric nitrogen and ammonia, but none were so good as the Ruffe, and except for the trouble of cleaning the tubes he would never have attempted to find another.

Many tests have been published showing the results obtained by this method compared with the theoretical ammonia, but, so far as the author is aware, none have been shown with a synthetical manure containing much chlorides.

The following may be of interest. A mixture was made as under:—

Parts.		Containing p.c. NH ₃ .		
9	dissolved bone manure ..	1.25	9 × 1.25 =	11.2
1	Belgian phosphate ..	—	—	—
1½	fish guano ..	10.41	1½ × 10.41 =	15.6
1½	Liebig's guano ..	8.62	1½ × 8.62 =	12.9
4	sulphate of ammonia ..	24.75	4 × 24.75 =	99.0
3	chloride of potassium ..	—	—	—
20			20)138.7	6.93

Two combustions by the ordinary method, using this special soda-lime, gave 6.97 and 7.03, mean 7.00 per cent.

Part.		Containing p.c. NH ₃ .		
0.8	of the above ..	7.00	0.8 × 7.00 =	5.60
0.2	pure nitrate of potash	16.83	0.2 × 16.83 =	3.36
				8.96

yielded 8.56 per cent by the modified Ruffe.

It will be observed that this contains much more nitrate than the usual run of manures, and one would therefore expect to get closer results in these cases.

Port Dundas Chemical Works,
Glasgow, May 6, 1890.

BORONISED SILVER.

By H. N. WARREN, Research Analyst.

THE element boron, when in its simplest form, presents no special affinity in general towards the non-oxidisable metals; but, by suitable means, the author has succeeded in combining variable amounts of from 5 to 6 per cent with metallic silver. This peculiar compound, of which I intend giving a brief description, first met my attention in endeavouring to reduce to the metallic state some residual argentic borate which had been specially prepared, containing an excess of free alkali, and intended for electrical research. On reducing this so prepared substance in contact with charcoal at a high temperature a button of metallic silver was obtained, which on close examination was observed to possess several abnormal properties; in so much that the colour of the same, when compared with a standard of pure silver, presented a decided yellow colour; at the same time, being less readily attacked either by the aid of acids or the vapour of sulphur. The presence of boron did not, however, strike me until a much later period, when I substituted for the above mixture one of potassium borofluoride, sodium, and scrap silver; on the application of a strong heat to the same, by the aid of an injector furnace, a button of silver possessing a decided yellow colour was obtained, and averaged about cupellation about 3 per cent difference. After several experiments were performed,

differing slightly from each other, I became influenced that pressure played a considerable part in aiding the combination of the boron, and as an improvement the following method was selected:—

Perfectly dried boric anhydride was obtained by the fusion of pure boracic acid, and intimately mixed with finely precipitated silver; to this was added a sufficiency of magnesium powder, and the whole introduced into a deep iron crucible, which was previously lined with charcoal, the same being provided with a heavy screw lid. The crucible and its contents were next raised and maintained at a white heat for half an hour; the silver thus obtained after extraction from its enclosure presented to all appearance an alloy of gold and silver, being with difficulty dissolved in nitric acid, and much less readily acted upon by the vapour of sulphur. A careful analysis of one of these buttons of so prepared silver showed the presence of 6 per cent boron.

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MANURE DRYERS.

By VINCENT EDWARDS, F.C.S.

THE object of the following experiments was to ascertain what effect, other than increase of weight and reduction of percentage of phosphate, &c., the addition of substances known as dryers has upon manures. They are added to the manure on removal from the "den" where it has been mixed, and are both for absorbing moisture and reducing the manure in value, so that the price may suit a section of the consumers. There is, of course, no objection to this; as a certain strength is usually guaranteed, but it seems a pity to use for this purpose anything that is detrimental to the manure and dangerous to the crop to which it is applied, especially when the remedy is easy. I have, from time to time, in testing super-phosphates noticed a reduction of strength and decrease of solubility greatly in excess of what would be due to the mere addition of inert chemical matter, and suspected this to be caused by soluble iron and alumina in the dryer. When in a soluble condition these elements are highly injurious to superphosphates, a fact which has been long known, and which renders many kinds of phosphate rock, of otherwise good quality, nearly useless. The ferric phosphate formed on addition of sulphuric acid is extremely insoluble in water, more so than tricalcium phosphate, while the same may be said of aluminum phosphate, though aluminum is not present in so large a quantity in phosphate rocks as iron. The artificial manure made is now so extensive and important that any facts tending to prevent mistakes and errors must be beneficial, and will, I hope, be taken as my apology for presenting the following results:—

I procured a quantity of high class superphosphate, made in the usual way from Norwegian phosphate rock of good quality. This superphosphate gave on analysis 12.7 per cent soluble P_2O_5 , equal to 27.72 $Ca_3P_2O_8$, or, to use the common way of expressing quality, 27.72 per cent "soluble phosphate." With this the experiments were made.

NO. 1 EXPERIMENT.—Cinders.—I obtained some cinders from steam coal; I believe they are frequently added to manures from the appearance of samples I have seen, which came from various parts of the country, the makers' names being unknown to me; some of them no credit to any manufacturer, and I am inclined to think some parties in the manure trade are not so straightforward as they might be. But the consumer is to blame if he will buy without an analysis of the principal ingredients, which is now so easily and cheaply obtained. The cinders gave on treatment with HCl, which I considered would extract at once all the soluble iron and

alumina, 12.0 per cent Fe_2O_3 , 1.4 per cent Al_2O_3 though a small quantity of the iron existed as FeS , H_2S gas being given off on the addition of HCl. I may mention, I find that when treating the insoluble portion of manures with HCl this gas is frequently noticed, and is a suspicious indication, as few phosphates contain any sulphide of iron, though iron pyrites may, of course, occur, and is not nearly so harmful, being quite insoluble in sulphuric acid. I made a mixture of nine parts of the superphosphate and one part of cinders, which certainly had the effect of rendering the manure very dry and friable. I allowed the mixture to stand for fourteen days, which is, I consider, about the time a superphosphate takes in getting from the "den" to the consumer, though it is often stored for weeks or even months, during which the conversion to $Fe_2P_2O_8$ and $Al_2P_2O_8$ is still going on. When analysed, the result of the mixture was 21.6 per cent soluble phosphate; this would indicate that the dryer had reduced the percentage of soluble phosphate by 5.12 per cent instead of 2.77 per cent, the reduction being due to the addition of 10 per cent of inert matter, a serious falling of in quality converting a really good superphosphate into a manure of the poorer class.

(To be continued).

SUMMARY OF USEFUL TESTS WITH THE BLOWPIPE.*

By A. J. MOSES.

(Continued from p. 225).

CARBONIC ACID, CO_2 .

With Nitric Acid.—Heat with water and then with dilute acid. CO_2 will be set free with effervescence. The escaping gas will render lime-water turbid.

With Borax or S. Ph.—After the flux has been fused to a clear bead, the addition of a carbonate will cause effervescence during further fusion.

CHLORINE, Cl.

With S. Ph. Saturated with CuO .—Treated at tip of blue flame, the bead will be surrounded by an intense azure-blue flame.

On Coal with CuO .—Grind with a drop of H_2SO_4 , spread the paste on coal, dry gently in O. F., and treat with blue flame, which will be coloured greenish blue and then azure-blue.

CHROMIUM, Cr.

With Borax or S. Ph.—O. F. reddish hot, fine yellow-green cold.

R. F. in borax, green hot and cold. In S. Ph., red hot, green cold.

With Soda.—O. F., dark yellow hot, opaque and light yellow cold.

R. F., opaque and yellowish green cold.

Interfering Elements.

Manganese.—The soda bead in O. F. will be bright yellowish green.

COBALT, Co.

On Coal, R. F.—The oxide becomes magnetic metal. The solution in HCl will be rose-red, but on evaporation will be blue.

With Borax or S. Ph.—Pure blue in either flame.

Interfering Elements.

Arsenic.—Roast and scorify with successive additions of borax. There may be, in order given:—Yellow (iron), green (iron and cobalt), blue (cobalt), reddish brown (nickel), green (nickel and copper), blue (copper).

* From the School of Mines Quarterly, vol. xi., No. 1.

Copper and other Elements which Colour Strongly.—Fuse with borax and lead on coal in R. F. The borax on platinum wire in O. F. will show the cobalt, except when obscured by much iron or chromium.

Iron, Nickel, or Chromium.—Fuse in R. F. with a little metallic arsenic, then treat as an arsenide.

Sulphur or Selenium.—Roast and scorify with borax, as before described.

COPPER, Cu.

On Coal R. F.—Formation of red malleable metal.

***Flame.**—Emerald-green or azure-blue, according to compound.

The azure-blue flame may be obtained—

(a) By moistening with HCl or aqua regia, drying gently in O. F., and heating strongly in R. F.

(b) By saturating S. Ph. bead with substance, adding common salt, and treating with blue flame.

With Borax† or S. Ph.—O. F., green hot, blue or greenish blue cold.

R. F., greenish or colourless hot, opaque and brownish red cold. With tin on coal this reaction is more delicate.

Interfering Elements.

†General Method.—Roast thoroughly, treat with borax on coal in strong R. F., and—

If Button Forms, separate the button from the slag, remove any lead from it by O. F., and make either S. Ph. or flame test upon residual button.

If no Visible Button Forms, add test lead to the borax fusion, continue the reduction, separate the button, and treat as in next test (lead alloy).

Lead or Bismuth Alloys.—Treat with frequently changed boracic acid in strong R. F., noting the appearance of slag and residual button.

Trace.—A red spot in the slag.

Over One Per Cent.—The residual button will be bluish green when melted, will dissolve in the slag and colour it red upon application of the O. F., or may be removed from the slag and be submitted to either the S. Ph. or the flame test.

FLUORINE, F.

Etching Test.—If fluorine is released it will corrode glass in cloudy patches, and in presence of silica there will be a deposit on the glass. According to the refractoriness of the compound the fluorine may be released—

(a) In closed tube by heat.

(b) In closed tube by heat and KHSO_4 .

(c) In open tube by heat and glass of S. Ph.

With Conc. H_2SO_4 and SiO_2 .—If heated and the fumes condensed by a drop of water upon a platinum wire, a film of silicic acid will form upon the water.

IODINE, I.

With S. Ph. Saturated with CuO .—Treated at the tip of the blue flame the bead is surrounded by an intense emerald-green flame.

In Matraass with KHSO_4 .—Violet choking vapour and brown sublimate.

In Open Tube with Equal Parts Bismuth Oxide, Sulphur, and Soda.—A brick-red sublimate.

With Starch Paper.—The vapour turns the paper dark purple.

Interfering Elements.

Silver.—The iodide melts in KHSO_4 to a dark red globule, yellow on cooling, and unchanged by sunlight.

IRON, Fe.

On Coal.—R. F., Many compounds become magnetic. Soda assists the reaction.

* Sulphur, selenium, and arsenic should be removed by roasting. Lead necessitates a gentle heat.

† By repeated slow oxidation and reduction a borax bead becomes ruby red.

‡ Oxides, sulphides, and sulphates are best reduced by a mixture of soda and borax.

***With Borax.**—O. F., yellow to red-hot, colourless to yellow cold.

R. F., bottle-green. With tin on coal, vitriol-green.

With S. Ph.—O. F., yellow to red hot, greenish while cooling, colourless to yellow cold.

R. F., red hot and cold, greenish while cooling.

State of the Iron.—A borax bead blue from CuO is made red by FeO and greenish by Fe_2O_3 .

Interfering Elements.

Chromium.—Fuse with nitrate and carbonate of soda on platinum, dissolve in water, and test residue for iron.

Cobalt.—By dilution the blue of cobalt in borax may often be lost before the yellow of iron.

Copper.—May be faded from borax bead by fusion with lead on coal in R. F.

Manganese.—(a) May be faded from borax bead by treatment with tin on coal in R. F. (b) May be faded from S. Ph. bead by R. F.

Nickel.—May be faded from borax bead by R. F.

Tungsten or Titanium.—The S. Ph. bead in R. F. will be reddish brown instead of blue or violet.

Uranium.—As with chromium.

Alloys, Sulphides, Arsenides, &c.—Roast; treat with borax on coal in R. F., then treat borax in R. F. to remove reducible metals.

LEAD, Pb.

On Coal.†—In either flame is reduced to malleable metal, and yields near the assay a dark lemon-yellow coat, sulphur-yellow cold, and bluish white at border.

With Bismuth Flux:—

On Plaster.—Chrome-yellow coat, blackened by $(\text{NH}_4)_2\text{S}$.

On Coal.—Volatile yellow coat, darker hot.

Flame.—Azure-blue.

With Borax or S. Ph.—O. F., yellow hot, colourless cold, flames opaque-yellow.

R. F. Borax bead becomes clear, S. Ph. bead cloudy.

Interfering Elements.

Antimony.—Treat on coal with boracic acid, and treat the resulting slag on plaster with bismuth flux.

Arsenic Sulphide.—Remove by gentle O. F.

Cadmium.—Remove by R. F.

Bismuth.—Usually the bismuth flux tests on plaster are sufficient. In addition, the lead coat should colour the R. F. blue.

LITHIUM, Li.

Flame.—Crimson, best obtained by gently heating near the wick.

Interfering Elements.

Sodium.—(a) Use a gentle flame and heat near the wick. (b) Fuse on platinum wire with baric chloride in O. F. The flame will be first strong yellow, then green, and lastly crimson.

Calcium or Strontium.—As these elements do not colour the flame in the presence of baric chloride, the above test will answer.

Silicon.—Make into a paste with boracic acid flux and water, and fuse in the blue flame. Just after the flux fuses the red flame will appear.

MAGNESIUM, Mg.

On Coal with Soda.—Insoluble, and not absorbed by the coal.

With Borax or S. Ph.—Clear and colourless, can be flamed opaque-white.

With Cobalt Solution.‡—Strongly heated becomes a pale flesh colour.

* A slight yellow colour can only be attributed to iron when there is no decided colour produced by either flame in highly charged beads of borax and S. Ph.

† The phosphate yields no coat without the aid of a flux.

‡ With silicates this reaction is of use only in the absence of colouring oxides. The phosphate, arsenate, and borate become violet-red.

MANGANESE, Mn.

*With Borax or S. Ph.—O. F., amethystine hot; reddens on cooling. With much, is black and opaque. If a hot bead is touched to a crystal of sodic nitrate, an amethystine or rose-coloured froth is formed.

R. F., colourless or with black spots.

With Soda.—O. F., bluish green and opaque when cold. Sodic nitrate assists the reaction.

Interfering Elements.

Chromium.—The soda bead in O. F. will be bright yellowish green instead of bluish green.

Silicon.—Dissolve in borax, then make soda fusion.

MERCURY, Hg.

With Bismuth Flux:—

On Plaster.—Volatile yellow and scarlet coat. If too strongly heated the coat is black and yellow.

On Coal.—Faint yellow coat at a distance.

† In Matrass with dry Soda or with Litharge.—Mirror-like sublimate, which may be collected in globules.

MOLYBDENUM, Mo.

On Coal.—O. F., a coat yellowish hot, white cold, crystalline near assay.

R. F., the coat is turned in part deep blue, in part dark copper-red.

Flame.—Yellowish green.

With Borax.—O. F., yellow hot, colourless cold.

R. F., brown to black and opaque.

With S. Ph.—O. F., yellowish green hot, colourless cold.†

R. F., emerald-green.

Dilute (½) HCl Solutions.—If insoluble, the substance may first be fused with S. Ph. in O. F. If then dissolved in the acid and heated with metallic tin, zinc, or copper, the solutions will be successively blue, green, and brown.

If the S. Ph. bead has been treated in R. F. the solution will become brown.

(To be continued).

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Continued from p. 222).

As regards the metals which are not precipitable by sulphuretted hydrogen in an acid solution, we must remark that the question here is generally the separation of iron, aluminium, and zinc in presence of calcium and magnesium phosphates. The author proceeds as follows:—

The hydrochloric filtrate from the sulphuretted hydrogen precipitate is strongly concentrated on the water-bath in a porcelain capsule, in order to expel sulphuretted hydrogen, mixed with chlorine-water, and evaporated to dryness. The residue is taken up with water, acidified with hydrochloric acid, filtered, the filtrate supersaturated with ammonia, the excess of ammonia nearly expelled by heating on the water-bath; the precipitate is filtered off, the ammoniacal filtrate is acidulated with acetic acid, and sulphuretted hydrogen is passed in at first at a boiling heat and afterwards until cold. The whitish precipitate of zinc sulphide is filtered off and weighed upon a filter. The precipitate upon the filter is dissolved in nitric acid, the solution is mixed with tin in a platinum capsule, and by repeated cautious treatment with nitric all the tin is converted into stannic acid, and hereby the phosphoric acid into insoluble stannic phosphate. The residue is

moistened with nitric acid, taken up in water, and left to settle in a beaker. The supernatant liquid is decanted off, and the precipitate is repeatedly treated with fresh portions of water containing nitric acid in order to extract the obstinate residues of alumina.

The filtrate is then concentrated, mixed with ammonia, the precipitate is filtered off and incinerated in a platinum crucible along with the filter. The ignited residue is fused for half an hour with sodium carbonate, prepared from the bicarbonate.

The melt, when cold, is lixiviated with water, let settle in a beaker, filtered, and in the filtrate the alumina is isolated and determined in the known manner.

c. Detection and Determination of Tin.

The alkaline filtrate from the sulphuretted hydrogen precipitate has still to be tested for the possible presence of tin. To this end it is acidulated with hydrochloric acid, boiled up, and H_2S is passed into the hot solution (which is turbid from the separation of sulphur) until it is cold, and it is then let settle in a moderately warm place for twenty-four hours. The precipitate is then filtered off, well washed with a solution of ammonium acetate, and incinerated along with the filter in a porcelain crucible. The residue is moistened with nitric acid, which is cautiously evaporated off, and the crucible ignited. As the residue always contains an admixture of ferric oxide, it is rinsed quantitatively with water into a silver crucible, the water is evaporated off, its last traces being expelled by gentle heating; caustic soda (prepared from metallic sodium, and dehydrated by previous re-melting) is added, and the mixture is kept in flux for half an hour.

The dark red heat prescribed in manuals of quantitative analysis is not necessary for this operation, and it merely occasions unnecessary damage to the crucible. The conversion of stannic oxide into sodium stannate is effected just at the melting-point of caustic soda.

When cold, the melt is lixiviated with water in the silver crucible, the contents are passed into a beaker and let settle. If a precipitate has been formed, it is filtered off, the filtrate is acidulated with hydrochloric acid, and the tin is precipitated in the usual manner with H_2S , and, finally, weighed again as stannic oxide.

Final Considerations on the Detection of Metals and Poisons in Organisms.

Among the metals normally present in the human organism must be included potassium, sodium, calcium, magnesium, iron, and manganese. In examining a human corpse, we, further, almost always find aluminium, copper, and zinc; more rarely, tin and lead; this circumstance should be kept in view. Generally we must remark that the quantities of the latter metals rarely exceed 10 mgrms. A distinction must be made whether the matter is found in the organs of a child or of an adult, though this point is more a question for the medical expert. The sources of these foreign metals occurring in small quantities in the human organism is the use of implements of iron, lead, zinc, and copper, as well as of foods and drinks, especially including beer. If a metal is detected, the question may arise whether it is a result of prolonged medical treatment or of chronic poisoning. This may be the case with lead, mercury, and especially with arsenic. As to aluminium, it may find its way into the organs of a corpse in the most varied manners, even after death. This will be intelligible if we reflect under what circumstances a *post mortem* is often conducted in villages and small towns, where dust and sand may lie on the tables and fall from the roof. Aluminium may occur in two places, both in the portion soluble and in that insoluble in hydrochloric acid, since if sand is treated with chlorine traces of alumina may be dissolved.

It is well known that organic substances which have been rendered soluble by treatment with chlorine are precipitated to a greater or less extent by H_2S , whether in an acid or an alkaline solution. Its removal by fusing the

* The colours are more intense with borax than with S. Ph.

† Gold-leaf is whitened by the slightest trace of vapour of mercury.

‡ Crushed between damp unglazed paper becomes red, brown, purple, or blue, according to amount present.

sulphuretted hydrogen precipitate with saltpetre is confined, according to general practice, to that part of the precipitate from an acid solution which is soluble in alkaline sulphides (arsenic, antimony, and tin). The fusion process is inapplicable to the other portion (insoluble and alkaline sulphides) on account of the possible presence of mercury; but as, according to the author's procedure, mercury is first sought for, and isolated if necessary, there is no objection to the fusion process.

The author conducts the demonstration of arsenic—in opposition to the practice which is probably universal—directly with the hydrochloric solution of the organic matter, and adopts the indirect way only if a preliminary examination has shown the presence of nitric acid in considerable quantities, or that of mercury or aniline colours.

(To be continued).

TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES.*

By F. A. GOOCH and F. W. MAR.

THE determination of chlorine associated with iodine in haloid salts is usually accomplished by differential or indirect means; either the two halogens are determined together in a portion of the assay, while the iodine alone is estimated in a second portion by one or other of well known methods, the difference between the sum of the halogens and the iodine being the chlorine sought; or, the silver salts of the halogens are weighed together and then converted into a single salt, or the metal, the ratio of chloride to iodide in the original salt being found by simple algebraic processes. If the amounts of iodine involved are minute, it is possible to separate that element by Fresenius's method of treatment with nitrous acid and a solvent like carbon disulphide, and then to determine chlorine directly in the residue; but the manipulation of the process is difficult, and the results inaccurate, when much iodine must be removed. The only method which has been deemed generally applicable to the direct estimation of chlorine associated with iodine in haloid salts is based upon Lassaigne's reaction, by which the iodine is precipitated as palladioid iodide; but the necessity of removing the excess of palladium by hydrogen sulphide before proceeding to precipitate the chlorine is so irksome that, even in this process, it is found to be more convenient to fall back upon the estimation of chlorine as the difference between the iodine found by the palladium process and the sum of the iodine and chlorine obtained by another test in another portion of the material. A straightforward and easy method for determining the chlorine is obviously desirable, and in the work of which we here give an account we have endeavoured to find such an one.

It is a well-known fact that when an aqueous solution of hydrochloric acid is boiled a point of concentration is reached, by the excessive loss of acid from stronger solutions and of water from weaker ones, at which for definite barometric pressure the liquid boils at a constant temperature and distils unchanged in composition. It follows naturally that a degree of dilution may be reached beyond which the loss of the acid must be inappreciable. Indeed, Fleischer justifies his use of hydrochloric acid as a standard in alkalimetric processes upon his observation that decinormal solutions of this acid, and even solutions of twice the strength (7.3 grms. to the litre), do not yield after ten minutes' boiling enough acid to redden blue

litmus-paper held in the steam. Hydriodic acid behaves similarly to hydrochloric in the matter of volatilising from aqueous solutions; but to the decomposing action of oxidising agents it is far more sensitive. Our endeavour has been to find conditions under which hydriodic acid may be completely broken up, and its iodine removed from the solution by vaporisation, while the hydrochloric is retained without appreciable loss. As a first step toward the solution of this question, we initiated a series of experiments upon the volatility of hydrochloric acid in solutions containing sulphuric acid, having fixed upon the latter as the most available means of liberating hydrochloric and hydriodic acids from their compounds with the alkaline metals. After a few preliminary experiments with litmus-paper exposed in the steam from boiling solutions, we settled down upon two modes of investigating this point. According to the first, the determination of the chlorine remaining after concentration in solutions made up of water, sulphuric acid, and known amounts of the chloride, by precipitating as silver chloride, filtering the precipitate on asbestos, and weighing, was made the test of volatility of the hydrochloric acid; in the second, the same object was accomplished by estimating the chlorine escaping from the solution, by passing the steam through a condenser and precipitating the acid in the distillate by means of silver nitrate, collecting and weighing the silver chloride as in the former method.

The experiments of series A to series F were carried out according to the first method. In them, portions of a dilute solution of potassium chloride of known value were measured from a burette into Erlenmeyer flasks of 500 c.m.³ capacity, sulphuric acid diluted one-half was added, and the solution was boiled until the flasks and contents removed from the flame and placed upon counterpoised scales just tipped the beam. A few trials sufficed to bring the weight to the required point, and the degree of concentration was determined by this means far more accurately than by lowering the level of the liquid to marks placed upon the flasks. The hydrochloric acid remaining after concentration was determined as described, the comparison of the result with the value of the standard solution of chloride indicating, of course, the total loss in the process.

In the experiments of Series A, B, C, D, the effect is traced of increasing proportions of chlorine as compared with the same amount of sulphuric acid taken. In those of Series C, E, F, the influence of changing proportions of sulphuric acid, while the amount of chlorine remains the same, is brought out. In both sets the evidence is plain that the volatility of the hydrochloric acid is dependent upon the proportion of sulphuric acid as well as upon the amount of the chlorine present. It appears likewise that when the amounts of sulphuric acid present are reasonably small the loss of hydrochloric acid is inconsiderable, if the concentration is not pushed to too great an extreme.

The quantities of chloride dealt with in the experiments (Series A to F) are rather smaller than those which would naturally be handled in practical analysis, so that it seemed best to extend the experimentation to solutions of greater dilution and containing larger amounts of chloride. In the experiments of Series G, and subsequently, the second mode of treatment referred to was adopted. The flask was filled as before, but was connected with an ordinary glass condenser so that the distillate might be collected and measured, and the hydrochloric acid condensed with the steam was estimated by precipitation as silver chloride, the last being dried and weighed as such upon asbestos. The details of the experiments are given in the tabular statement (Series G).

It is obvious from these results that a solution containing 10 c.m.³ of the 1:1 sulphuric acid, or 5 c.m.³ of the strong acid, may be concentrated 200 c.m.³ without significant loss of hydrochloric acid. At a concentration of 100 c.m.³ the loss is notable. In later experiments, we

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., April, 1890.

† Roscoe and Dittmar, *Quart. Jour. Chem.*, xii., 128.

Series A.							
Taken H_2SO_4 [1:1]. C.m.s.	Taken KCl = HCl.		Found AgCl = HCl.		Initial volume. C.m.s.	Final volume. C.m.s.	Error. Grm.
	Grm.	Grm.	Grm.	Grm.			
10	0.05	0.0245	0.0963	0.0245	110	5	0.0000
10	0.05	0.0245	0.0957	0.0243	110	45	0.0002-
10	0.05	0.0245	0.0945	0.0240	110	40	0.0005-
10	0.05	0.0245	0.0941	0.0239	110	35	0.0006-
10	0.05	0.0245	0.0871	0.0221	110	30	0.0024-
10	0.05	0.0245	0.0821	0.0209	110	25	0.0036-
Series B.							
10	0.1	0.0489	0.1910	0.0485	110	65	0.0004-
10	0.1	0.0489	0.1922	0.0488	110	55	0.0001-
10	0.1	0.0489	0.1908	0.0485	110	45	0.0004-
10	0.1	0.0489	0.1894	0.0482	110	35	0.0007-
Series C.							
10	0.2	0.0978	0.3887	0.0976	110	75	0.0002-
10	0.2	0.0978	0.3838	0.0976	110	65	0.0002-
10	0.2	0.0978	0.3831	0.0974	110	55	0.0004-
10	0.2	0.0978	0.3816	0.0970	110	45	0.0008-
10	0.2	0.0987	0.3746	0.0953	110	35	0.0025-
10	0.2	0.0978	0.3322	0.0845	110	25	0.0133-
Series D.							
10	0.4	0.1956	0.7690	0.1955	110	60	0.0001-
10	0.4	0.1956	0.7682	0.1954	110	50	0.0002-
10	0.4	0.1956	0.7574	0.1926	110	35	0.0030-
Series E.							
5	0.2	0.0978	0.3845	0.0978	105	55	0.0000
5	0.2	0.0978	0.3838	0.0976	105	45	0.0002-
5	0.2	0.0978	0.3823	0.0972	105	35	0.0006-
5	0.2	0.0978	0.3788	0.0963	105	25	0.0015-
Series F.							
20	0.2	0.0978	0.3782	0.0962	120	75	0.0016-
20	0.2	0.0978	0.3602	0.0916	120	65	0.0062-
20	0.2	0.0978	0.3087	0.0785	120	55	0.0193-
20	0.1	0.0978	0.2931	0.0745	120	45	0.0233-
Series G.							
Taken H_2SO_4 [1:1]. C.m.s.	Taken KCl = HCl		Initial volume. C.m.s.	Final volume. C.m.s.	Time in minutes.	Found AgCl. Grm.	Loss of HCl. Grm.
	Grm.	Grm.					
10	I	0.4888	400	300	29	0.0005	0.0001
10	I	0.4888	400	300	22	0.0008	0.0002
10	I	0.4888	350	300	10	0.0004	0.0001
10	I	0.4888	350	300	9	0.0005	0.0001
10	I	0.4888	300	200	25	0.0008	0.0002
10	I	0.4888	200	100	27	0.0021	0.0005
10	I	0.4888	100	50	20	0.0037	0.0009

found that a small part of the precipitate which we weighed in these experiments must in reality have resulted from the action of the solution upon the rubber stoppers and connectors of the apparatus; for the distillate from pure water in the same apparatus yielded a precipitate, probably silver sulphide, which, filtered off and weighed, was found to amount to 0.0003 grm. The figures of Series G, therefore, overstate somewhat the volatility of hydrochloric acid under the circumstances, but the misrepresentation is inconsiderable. We fixed upon 300 c.m.³ as a convenient volume of liquid to manipulate in future experiments, and one sufficiently dilute to guarantee security against the volatilisation of hydrochloric acid when the amount of sulphuric acid does not exceed 5 c.m.³ of the strong acid, and when the quantity of potassium chloride present does not exceed 1 grm.

(To be continued).

ON THE ESTIMATION OF WATER IN PHENOL.

By J. A. WILSON.

A SAMPLE of crude carboic acid (*i.e.*, the liquid remaining after crystallisation of true phenol, and consisting of cresol and higher homologues), when tested by three methods—(No. 1) by distillation; (No. 2) by agitating 1 vol. with 3 vols. saturated salt solution; (No. 3) by agitation with equal vols. of 48–50 per cent hydric sulphate—gave the following results:—

	No. 1.	No. 2.	No. 3.
Water ..	8.6 per cent.	8.00 per cent.	8.25 per cent.

The distillation process gives the true percentage of water, if the distillate be not observed too late; next to this the test with vitriol.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, May 1st, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MESSRS. Joseph Barker and Thomas Flower Ellis were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Wallis Jenkins, 9, Arnold Street, Anlaby Road, Hull; John McKillop, Pulan Brani, Singapore; John Brooks Thornley, Ivanhoe Terrace, Ashby-de-la-Zouch.

The following papers were read:—

33. "An Investigation of the Conditions under which Hydrogen Peroxide is formed from Ether." By Professor WYNDHAM R. DUNSTAN and T. S. DYMOND.

The authors have investigated the conditions under which hydrogen peroxide is formed from ether. The ether used by them was purified by the usual method, and also by repeated agitation with dilute aqueous chromic acid.

Contrary to the usual statement, the authors find that pure ether, either wet or dry, does not form hydrogen peroxide when exposed to light (daylight or electric light).

Ether prepared from methylated spirit yields hydrogen peroxide when kept for some time, but not if it has been previously purified by means of dilute chromic acid.

Neither water nor dilute sulphuric acid forms hydrogen peroxide when exposed to light in contact with air.

Hydrogen peroxide is formed when ozone acts on ether in the presence of water.

Hydrogen peroxide is produced when certain conditions are maintained during the slow combustion of ether in contact with water. At a low red heat the ether and oxygen appear to interact in a manner similar to that in which ozone and ether interact.

DISCUSSION.

Dr. RICHARDSON said that everything depended on the nature of the glass of the bottles in which the liquids were exposed, and the quality of the light. The authors had spoken of Winchester bottles. Of what kind of glass were the bottles which had been used made? With regard to the method which he had adopted in purifying his ether, so-called pure ether was shaken with water, and then repeatedly distilled from sodium until at last this was unaffected. His more recent experiments led him still to believe that peroxide was formed from water and oxygen on exposure to light.

Professor RAMSAY, speaking of the purification of ether, referred to the investigation of the thermal properties of ether by Professor Young and himself. Regnault states that ether, after standing, no longer has a constant boiling-point, and they had found that such ether acts on mercury, but that after agitation with mercury and distilling it does so no longer. Professor Young and he had prepared ether from alcohol and sulphuric acid, and after washing it with potash and with sulphuric acid, had found it necessary to agitate it about fifty times with water before the iodoform test ceased to afford evidence of the presence of alcohol. Proof that such ether was pure was afforded by the agreement of the determinations of its vapour pressure made by the static and dynamic methods; four specimens were found to give identical results. Some of the authors' specimens may have contained alcohol. He then referred to the experiments which he had made showing that hydrogen peroxide is produced on evaporating water (*Proc. Chem. Soc.*, 1886, 225).

Mr. WOOD asked if any observations had been made of the temperature during exposure; the amount of ether vapour would vary greatly with the temperature. In India he had frequently noticed that ether liberated iodine, but its behaviour in this respect was extremely capricious;

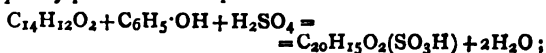
he could scarcely think that the very different behaviour of several bottles of one consignment was due to impurity.

Professor DUNSTAN, in reply to Dr. Richardson, stated that colourless Winchester bottles were employed. The specimen of impure ether which yielded hydrogen peroxide scarcely affected potassium iodide before exposure; another similar specimen had no action on the iodide. He had not been able to confirm Dr. Richardson's statement that hydrogen peroxide is formed when acidified water is exposed to light together with oxygen. In reply to Dr. Ramsay, he stated that the method used to purify the ether must have resulted in the entire removal of alcohol. The experiments now recorded proved that under certain well-defined conditions hydrogen peroxide was not formed from pure ether. It was for those who, like Dr. Richardson and Professor Ramsay, maintained that it is produced under similar circumstances to point out what the necessary condition is. This had not yet been done, and in fact so far apparently no one had suspected that the result might be due to an impurity. He had not been able to detect any hydrogen peroxide in water which had been heated in the manner described by Professor Ramsay in contact with air, although the experiment had been tried many times. With reference to Mr. Wood's remarks, the conditions under which the ether had been exposed were fully described in the paper; the temperature ranged between 15—25°. In London it was not possible to obtain "intense sunlight," but it seemed well established that the electric light is highly active in influencing chemical change. There was evidence that ether prepared from ordinary alcohol sometimes, but not invariably, contains the impurity from which hydrogen peroxide is formed; in any case this impurity would be removed by treatment with chromic acid. As was stated in the paper, the formation of an oxidising substance by the imperfect combustion of ether, to which Mr. Wood had referred, had been observed long ago: in fact Faraday had shown the experiment in his lectures on ozone. It is established by the present results that pure ether yields hydrogen peroxide when it is imperfectly oxidised in contact with cold water.

In reply to the President, he said that, although the period of exposure was the same in the case of the experiments with purified ether, they were made at a later date.

34. "*p*-Desylphenol." By FRANCIS R. JAPP, F.R.S., and G. H. WADSWORTH, Associate of the Normal School of Science.

The authors find that by the action of cold concentrated sulphuric acid on a mixture of benzoïn and phenol *p*-desylphenol-monosulphonic acid is formed:—



and that on heating this with concentrated chlorhydric acid at 150° it is hydrolysed, yielding *p*-desylphenol, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. This phenol crystallises from light petroleum in small colourless laminæ melting at 133°; from dilute alcohol in large thin laminæ; and from benzene in warty aggregations with 1 mol. of benzene of crystallisation. It dissolves in caustic alkalies, and is re-precipitated by carbon dioxide.

When heated with acetic anhydride it yields a monacetyl-derivative, $\text{C}_{20}\text{H}_{15}(\text{C}_2\text{H}_3\text{O})\text{O}_2$, which forms aggregations of slender white needles melting at 106—107°.

By acting on the sodium salt with methyl iodide, *p*-desylanisole, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3$, is obtained. It melts at 90—92°, and is insoluble in caustic alkalies.

On fusion with caustic potash at 200°, *p*-desylphenol is resolved into benzoic acid and *p*-benzylphenol. If the temperature be carried higher the *p*-benzylphenol is oxidised to *p*-hydroxybenzoic acid. On reduction with sodium and boiling amyl alcohol, it is converted into the compound $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, which

Since each inclined section is subject to the same total shearing force, the shearing stress along any section such as EF may be taken as inversely proportional to the length of the line EF , the bar being supposed of uniform thickness. From these considerations it may be seen that an element, F , will be subject to equal stresses, for $AB = OD$; hence the lower point of F will remain vertically below its upper point. In this region, therefore, a horizontal straight line drawn on the unstrained bar will remain horizontal and straight on the strained bar. An element at Q , however, will be subjected to unequal stresses, for $EF < QH$; hence the lower points of the elements will be displaced towards the axis. This displacement will increase as the distance beyond d and e from the axis increases, and an originally horizontal line will become curved at the ends cd and ef , whilst de will remain straight. In a similar way it was shown that horizontal lines should assume the shapes indicated at ghi , $jklmn$, opq , rst , and uvw in their respective positions, whilst vertical lines should become pinched inwards above and below the shoulder, as shown by the curve $wxyz$. To test whether the reasoning by which the above conclusions were arrived at was satisfactory, a copper bar was carefully prepared, ruled, and subjected to permanent strain. The curvatures of the various lines clearly show the characteristics predicted by theory.

Prof. PERRY enquired whether it was correct to assume the stress uniform over the plane sections inclined at 45° to the axis. He also said that the general character of the flow somewhat resembled that of a viscous fluid passing from a wide to a narrower channel.

Prof. HERSCHEL thought Mr. Carus-Wilson justified in assuming the stress uniform over the diagonal sections; the latter said he only made the assumption as a provisional hypothesis, but the results of his experiment agreed so closely with his theoretical deductions that he thought the hypothesis correct.

Mr. C. V. BOYS made two communications:—(1) "*On Photographs of Rapidly Moving Objects*," and (2) "*On the Oscillating Electric Spark*."

A collection of apparatus by which he had been able to photograph drops of water in their various stages of formation was exhibited. It consisted of a lantern and lenses by which a trough in which the drops were formed could be strongly illuminated, combined with a camera and revolving disc with one perforation. By this means exposures of about 1/600th of a second could be made about 20 times a second. The slide of the camera was about 3 feet long, and could be moved across the field by hand, so as to take the consecutive impressions on different parts of the plate. The resulting photographs show with remarkable clearness the formation, breaking away, the oscillations of the drops, and their rebounding in the liquid into which they fell. By cutting the photographs into strips, each strip representing a single exposure, and mounting them on a disc, Mr. Boys had arranged a kind of Thaumatrope, which represented the phenomena in a very realistic manner. He also exhibited photographs of small water-fountains broken up into drops by musical sounds, which he had taken by the electric spark without the aid of lenses. The shadows of the drops were sharply defined, even when magnified considerably, and the various stages of transition from the liquid column to the detached particles were well shown. Finding it possible to obtain such good results from a simple spark, it occurred to him that he might get a succession of photographs from the intermittent light of an oscillating spark, and in this he was fairly successful.

An apparatus devised to show the oscillatory character of a discharge was next exhibited in operation. It consisted of a disc carrying six lenses arranged in two sets of three. The members of each set were at different distances from the axis, so that the images of the spark on the screen do not coincide. The disc can be revolved at a high speed, and the successive sparks are seen as bright patches on the screen. By this apparatus a single

discharge can be examined, whereas with Lodge's apparatus it is desirable to have a fairly rapid succession of sparks. Photographs of an oscillatory discharge taken with the apparatus were exhibited, and these show that the duration of the illumination is a considerable fraction of a complete period.

LORD RAYLEIGH said he was greatly interested by Mr. Boys' apparatus. He (Lord Rayleigh) had photographed water-fountains both when broken up and when made to coalesce under electrical influence, but it had never occurred to him that it would be possible to get enough light or sufficient sharpness from a single spark. Mr. Boys' success he believed to be owing to the fact of his using no lenses which would absorb the ultra-violet rays. He also thought the method might be developed so as to give shaded pictures instead of mere representations in black and white.

Mr. GREGORY asked Mr. Boys if he had tried to get greater potentials for his oscillatory discharges by using Dr. Lodge's "impulsive rush" arrangement.

Mr. TROTTER enquired whether the single sparks used to photograph the water fountains were as large as those required to show oscillations.

Mr. BOYS said he had not tried Dr. Lodge's "impulsive rush" arrangement because of the enormous capacity of the condensers required. The sparks used to photograph the broken up fountain were very small, being only about 1/4-inch long and from a few jars.

Prof. PERRY asked Lord Rayleigh whether it would be possible to compare the shapes of the water-drops shown in the photographs with the shapes of the liquid surfaces of revolution given by Sir W. Thomson at the Royal Institution some years ago, or whether the changes of shape were too rapid to permit of the surface-tension being all-important.

Mr. BOYS thought the motions of the drops would be too rapid, and that inertia would play an important part.

LORD RAYLEIGH pointed out that by forming a drop slow enough the effect of inertia might be made negligible until such time as the unstable state was reached; after that, however, inertia must have considerable influence on the shape.

NOTICES OF BOOKS.

Report of the Commissioner of Internal Revenue for the Fiscal Year ended June 30, 1889. Washington: Government Printing Office.

A GREAT part of the contents of this book have for us no interest, but there are portions relating to the sophistication of articles of food, &c., which are of considerable importance.

Baking-powders are denounced as "the make-shift of the lazy and ignorant bread-maker." They all convey into the system "medicinal doses" of various salts. Of course what is called a medicinal dose must be hurtful if habitually consumed in food. A list is here given of manufacturers of "alum baking-powders." It is satisfactory to find that only one British firm figures in this numerous catalogue, and that it does not bear a name familiar in this country.

"Package coffee," meaning the article sold ready-ground, is heavily tampered with; chicory, peas, beans, rye, maize, wheat, and colouring matters rank as the common adulterants.

Cream of tartar is sophisticated with gypsum, acid calcium phosphate, calcium tartrate (more than 6 per cent), alum, maize, starch, and flour.

Tinned vegetables, all supplied by French firms, are coloured with copper sulphate.

The use of annatto for colouring butter and cheese is open to very grave objections. Dr. B. F. Davenport says, in a report to the State Board of Health of Massachusetts,

1888, "That prepared in French Guiana is considered the superior brand of the dye-stuff. There, in the warehouses, it is reported to be the general commercial custom to improve the colour of the dye-stuff, and prevent its drying by keeping the cake moistened with stale urine (!). The result is that it is a mass of fermentative products, swarming with germs of putrefaction, and smelling rankly of its origin. . . . Microscopic examination shows that it is not only alive with bacteria, but that it contains very numerous fungi spores, single or arranged in rows like those found in fermented diabetic urine." Of course the possible presence of pathogenic bacteria in daily produce thus coloured is by no means excluded.

University of Illinois, Agricultural Station, November, 1889,

We have here a paper on the "Biology of Ensilage," in which the admission is made that ensilage is never truly preserved fodder. The author remarks, truly enough, that the main difference between ensilage and sour-kraut is that the former is made from clover, &c., and the latter from cabbage.

The rest of the pamphlet describes field experiments on oat and maize.

Exercises in Practical Chemistry: An Introduction to Qualitative and Quantitative Analysis. By Dr. W. R. HODGKINSON, F.R.S.E., F.G.S. London: G. Kenning. Third Issue, revised.

THIS little work, we are told, is a reprint from sheets that have been used with considerable success in the instruction of large classes. We find in it no errors, but, on the other hand, we cannot recognise that it possesses any marked advantage over other elementary treatises on chemical analysis.

Terminologia Medica Polyglotta: A Concise International Dictionary of Medical Terms. Compiled by THEODORE MAXWELL, M.D., B.Sc., F.R.C.S. London: Churchills.

THIS work is, we believe, unique in its character and aims. It is, in fact, a polyglot dictionary of the technical language of the medical profession in English, French, Latin, German, Italian, Spanish, and Russian. The terms included are those of anatomy and physiology (human, not general), nosology, pharmacy, chemistry, and, to some extent, physics. Botany is also very fully dealt with. The technical language of zoology is introduced only in the case of venomous and parasitic animals, and of such as furnish medicinal drugs. These various subjects are not taken up separately, the only arrangement adopted being alphabetical.

As far as we can judge the work is characterised by a very high degree of correctness.

The only questionable points are, we believe, to be found in the chemical department. The compiler and his friends have retained for the English names of compounds a terminology which is fast becoming obsolete. Thus, e.g., they write "iodide of iron" where in recent works and memoirs we find almost exclusively "iron iodide," or, if it is desired to be more precise, "ferrous" or "ferric iodide."

Among German chemical terms "potassium" is rarely, if ever, used, its German equivalent being "kalium." In like manner "sodium" and "soda" are rarely used in Germany, save in purely technological works, the scientific equivalents being "natrium" and "natron."

It might have been usefully pointed out that the chemical terms used by physicians and pharmacists in Germany are sometimes widely different from those employed by "pure" chemists and manufacturers, being, in fact, taken from the Latin! Thus a German analyst, researcher, or University professor would call potassium chloride "chlorkalium," whilst in a prescription or in a

pharmaceutical catalogue the same compound would figure as "kalium chloratum."

It would be unpardonable to omit notice of the wonderful typographical accuracy of this book. In a volume of nearly 500 pp., consisting exclusively of technical matter, and that, moreover, mostly written in foreign languages, we have not been able to meet with any errors of the press. Of course, to the medical profession this work will be of untold value, throwing open to them the literature of most other civilised countries.

Agenda du Chimiste (Chemists' Manual). By G. SALET, Ch. GIRARD, and A. PABST, 1890. Paris: Hachette et Cie.

THIS is a new edition of a useful pocket volume brought down to the present date. It begins with an almanac in which the mediæval "Saints' Days" figure in juxtaposition with the meetings of the Chemical and Physical Societies. Next follows a chapter devoted to physical and mathematical data, and containing, amongst other matters, tables for the reduction of English measures and weights to their metric equivalents. In hydrometry, the scale of Baumé with all its imperfections is still adhered to, though it appears to exist in four modifications. Instruments indicating direct specific gravity do not seem to find much favour in France, and Twaddle's scale is very briefly noticed. The tables of the specific gravities of acids and saline solutions are numerous and valuable.

Thermo-chemistry is treated, as might be expected, at considerable length.

In the second chapter, follow data relative to pure chemistry. The tables of atomic weights are somewhat complex; there are firstly the equivalents and atomic weights of the more common bodies, as they have been adopted in Fremy's "Encyclopédie Chimique," the atomic weights used in the first edition of the "Agenda," and that from the edition of 1886, and lastly the atomic weights arrived at by the most recent researches. Then follow tables for qualitative analysis in the moist way, and tables for blowpipe analysis, with explanatory remarks. No mention is made of the use of the aluminium plate as a support.

A short section is devoted to spectral analysis, attention being principally given to spark-spectra. Absorption-spectra are described and figured in a section of the appendix on p. 462.

Next follows gas-analysis; tables for calculating the results of quantitative analysis; a long table giving the composition and the solubility of the principal inorganic bodies, with brief notes on their other properties; tables of the composition and external characters of minerals, their density, hardness, solubility, fusibility, and crystalline form; the composition and properties of organic bodies; and tables of solubilities.

The third chapter relates to applied and industrial chemistry. It opens with a section on water analysis, in which we find that, as far as the determination of organic nitrogen is concerned, the process of Frankland is ignored, and that of Wanklyn meets with a very momentary notice. The comparison between English, French, and German degrees of hardness is a very useful hint. We cannot agree with the authors when they say that the only waters for consumption are those of underground beds and of streams. The rejection of rain-water is imperative only in districts where the air is polluted or where it is collected on roofs, &c., visited by cats and pigeons, both possible vehicles of diphtheria. We may here add that dogs should be rigorously excluded from the gathering grounds of a municipal water-supply, as they introduce the germs of hydatids.

The bacteriological examination of waters is here spoken of as yielding merely uncertain results. But in the appendix it is discussed at length, and pronounced of great importance.

The instructions for the analysis of a variety of com-

mercial and industrial articles are carefully drawn up, and will often be useful for refreshing the memory of the analyst.

Doubts may be entertained whether the space devoted to a review of the Paris Exhibition might not have been better occupied.

We may notice the suggestions of an International Congress of Chemists on the question of nomenclature. It is satisfactory to find that they propose to reserve the termination "ol" for the alcohols and the phenols, and applying, in its stead, the termination "ene" to the hydrocarbides. It would be better still if the terminations "in" and "ine" could be dispensed with, since they have been seized upon by the inventors of "proprietary" medicines and applied to compounds which, whatever may be their medicinal value, are certainly not chemical individuals. "Listerine" is a name which sets our teeth on edge.

The "Agenda du Chimiste" is a very useful work-table companion.

CORRESPONDENCE.

EXTENSION OF THE DUTIES OF PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—I have read with much pleasure your review upon Mr. C. E. Cassal's paper upon the extension of the duties of public analysts, in the CHEM. NEWS, vol. lxi., p. 226.

It cannot, I think, be for one moment contended that the extension of their duties would not be desirable—all, I think, are agreed upon that point; but if their duties are to be extended, the present Sale of Food and Drugs Act ought to be entirely replaced by a new Act, the public analyst of to-day abolished, and his place taken by a Government or a State analyst.

The present Act, where it has been properly enforced, has done much to check adulteration, and, if equally enforced throughout the country, would do much good—but such a result, however desirable, will never be attained. The powers conferred upon local authorities to appoint analysts ought to have worked well, but, unfortunately, latterly the most competent and experienced candidates have been rejected for young and inexperienced ones, simply on account of local patronage. Then again, there are analysts in London at the present moment holding appointments under the Act contrary to Section 10 (C) of the Sale of Food and Drugs Act, 1875.

What is now required is a new Act establishing a State laboratory, say, under the control of the Minister of Agriculture, with full powers to analyse the food, drink, and drugs of the country, and a clause also inserted in the Act giving power to the Minister of Agriculture to include or bring under the scope of the Act from time to time any article which is not included under the term food, drink, and drugs, if it should be deemed advisable to do so.—I am, &c.,

WILLIAM JOHNSTONE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 17, April 28, 1890.

Formation and Combustion-Heats of Various Nitrogenous Principles derived from Albumenoid Matters.—MM. Berthelot and André.—The substances

studied are glycollamine, alanine, leucine, asparagine, aspartic acid, tyrosine, and hippuric acid.

Researches on the Condensation of the Vapour of Benzene and of Acetylene under the Influence of the Effluve.—P. Schützenberger.—The ultimate object of these researches is to determine the question of the permeability of the effluve. Whilst the benzene used contained 92.47 per cent of carbon and 7.80 of hydrogen, the condensed products showed from 0.7 to 7.0 per cent of oxygen.

Lead Phosphites and Pyrophosphite.—L. Amat.—An account of neutral lead phosphite, of the nitrophosphite, the acid phosphite, and pyrophosphite.

Action of Erythrite upon the Alkaline Alcoholates.—M. de Forcrand.—A thermo-chemical paper, not suitable for abstraction.

Action of Lead Oxide upon Toluene; Production of Benzene.—C. Vincent.—The products of the reaction as obtained by the author were about 10 per cent of benzene, a small quantity of stilbene, and a residue of toluene not attacked, as well as water and carbonic acid. At temperatures exceeding 335° there was less benzene and more stilbene and higher carbons. At redness there were obtained, along with the above products, the carbides, formed on a simple pyrogenous decomposition of benzene and toluene. The diphenyl formed in small quantity is not derived from benzene originally present in the toluene, but from benzene formed in the reaction.

Thermo-Chemical Researches on the Fibres of Wool and Cotton.—Leo Vignon.—The author gives the quantities of heat in calories evolved respectively by wool and cotton in contact with different reagents.

Zeitschrift für Analytische Chemie.
Vol. xxviii., Part 6.

New Test for Carbon Oxide Hæmoglobine.—K. Katayama (*Virchow's Archiv*).—10 c.c. of the blood diluted to 150th are added to 0.2 deep yellow ammonium sulphide and 0.2–0.3 c.c. of a 30 per cent acetic acid, and carefully mixed. The liquid should then react slightly acid. Blood containing carbon monoxide takes a fine rose colour, whilst normal blood is greenish grey or reddish greenish grey. The ammonium sulphide is obtained by adding 2.5 grms. of pure pulverised sulphur to 100 grms. of freshly prepared colourless ammonium sulphide. A spectroscopic examination of the carbon monoxide blood treated as above shows the spectrum of sulphmethæmoglobine (an absorption band between C and D) along with that of the carbon monoxide hæmoglobine. Normal blood under the same conditions shows, along with the sulphmethæmoglobine stripes, the broad absorption-band of reduced hæmoglobine, which, on shaking with air, gives place to the two absorption-bands of air. The presence of such blood can be recognised along with seven parts of normal blood.

Poisoning with Barium Salts.—G. Linossier.—The author detects barium in all the organs; up to 0.56 per cent in the ash of the vertebrae.

Distinction between Nepalin and Aconitine.—K. F. Mandelin.—Nepalin, if evaporated down with a few drops of strong nitric acid, gives a residue smelling of musk. This residue, if treated with a few drops of a solution of potassa in absolute alcohol, gives an intense carmine or purple. Aconitine is quite indifferent in its behaviour.

The Atomic Weight of Platinum and Rubidium, and on Quantitative Determinations with the Help of Platinum Chloride.—W. Dittmar and J. McArthur.—From the Transactions of the Royal Society of Edinburgh.

Poisoning with Oxalic Acid.—Russo-Gilberti (*Apotheker Zeitung*).—Crystals of calcium oxalate are found blocking up the ducts of the kidneys.

MEETINGS FOR THE WEEK.

- MONDAY, 19th.—Society of Arts, 8. "Sugar, Tea, Coffee, and Cocoa, their Origin, Preparation, and Uses," by Richard Bannister.
- TUESDAY, 20th.—Royal Institution, 3. "The Art of Engraving—3. Mezzotint Engraving," by Louis Fagan.
- Institute of Civil Engineers, 8.
- Pathological, 8.30.
- Society of Arts, 5. "The Industrial Arts of Japan," by Lasenby Liberty.
- WEDNESDAY, 21st.—Society of Arts, 8. "The Mannesman Process for Making Seamless Tubes," by J. G. Gordon.
- Meteorological, 7.
- Geological, 8.
- Pharmaceutical, 11. (Anniversary).
- THURSDAY, 22nd.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
- Royal, 4.30.
- Royal Society Club, 6.30.
- Institute of Electrical Engineers, 8.
- FRIDAY, 23rd.—Royal Institution 9. "The Manners and Customs of the Torres Straits Islanders," by Prof. A. C. Haddon, M.A., M.R.I.A., Dean of Royal College of Science, Dublin.
- Quckett Club, 8.
- SATURDAY, 24th.—Royal Institution, 3. "Recent Excavations in Greece," by Dr. Charles Waldstein.

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Chemiker-Zeitung.

(EDITOR: DR. G. KRAUSE, COTHEN, DEUTSCHLAND.)

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THE CHEMICAL NEWS.

VOL. LXI. No. 1591.

CORROSION OF PLATES OF STEAM-BOILERS.

By THOMAS T. P. BRUCE WARREN.

THE *inside* corrosion of the iron plates of a steam-boiler is due at least to two causes; in one case the corrosion, indicated by *pitting*, takes place above the water line, and in the other case by *patches* on the surface covered by incrustation or deposit. In both cases there is a marked absence of uniformity of corrosion, some plates being seriously affected, whilst others in the same boiler and in the same region of the boiler remain intact. This has been explained by the heterogeneous character of the plates, due either to chemical or mechanical differences.

It certainly requires no great amount of chemical skill to determine how far these factors operate in shortening the life of a boiler. A matter which appears to me to have escaped the attention of writers on this subject deserves mention. It is well known that a rolled iron plate has a "skin" or surface which resists oxidation; if we remove this, by scratching or filing, the new surface is rapidly coated with rust on exposure to damp air. If we protect with a varnish those new surfaces corrosion is not perceived. If a freshly rolled plate be cut the surface remains intact, whereas the edges rust in a very short time. If a piece of sheet-iron be immersed in dilute acid the surface, coated with what is known as the natural skin, resists the action more or less, whilst the recently cut surfaces are speedily acted on.

This is no doubt due to a difference in the electrical relation of the surfaces, the one being much more electro-positive than the other. The aggravation of pitting, which is not only local, but, in some parts of the same plate, serious, can be explained in the same way.

In the construction of a boiler there are several operations which destroy the uniformity of surface; the rivets, the holes, whether punched or drilled, all introduce an individual function in the wear and tear of a boiler. The natural skin of an iron plate, if partly removed, exposes a surface which is electro-positive to the other parts, and, when placed in a corrosive liquid, the parts of the plate which are electro-negative actually assist in the destruction of the parts which are less electro-negative; hence it is that pitting is promoted when it once sets in.

The only remedy seems to be the entire removal of the surface after rolling; we might then ensure an uniform surface, when alteration or abrasion would be less likely to lead to local chemical action.

The utility of the magnet for determining inequalities in a boiler plate seems to me very problematical, but the difference of potential when two plates are immersed in the same liquid, as might be observed on an electrometer, would reveal the existence of chemical or mechanical differences of structure which would be favourable to corrosion.

It has been proposed to use zinc as a protection against corrosion; and no doubt, by rendering the boiler surface electro-negative, we might prevent corrosion, but unfortunately the instructions given for its use are misleading. In some cases pieces of zinc are simply thrown into a boiler, so long as they remain *clean* and are in contact with a *clean* boiler plate, the preservative action of the zinc is ensured, but when covered with mud or boiler deposit, they are shielded from further action. If the zinc be suspended or attached *metallically* to the boiler, above the water line, we are more likely to prevent corrosion from volatile acids, the iron being electro-negative to zinc.

The corrosion of the zinc being greatest at the points of suspension, it will in time wear away and fall into the deposit, where it becomes, in an electro-chemical sense, lost, but, so long as it remains suspended, the wear and tear at the points of attachment keep the contacts clean. We must remember that the greatest loss of zinc is where the metallic contacts lie, and that by increasing the area of the zinc plate, so long as the area of contact is constant, we are doing little or no good. The ratio between the areas of contact of the two metals, so as to ensure the maximum advantage, when once determined for any particular water should be most rigidly enforced. When a boiler is cleaned out it is the practice to "put the zinc back again;" clean contacts or drilling fresh holes in the zinc plate if worn much should never be neglected. The surface of the plate should be entirely renewed. It is well known that no metal should be allowed to introduce an electro-positive condition of the boiler-plates. Spelter or sheet-zinc frequently contains a large quantity of lead; in time the zinc dissolves away, leaving a surface richer in lead; we are then in a fair way of doing more harm than good to our boiler plates, in spite of the solubility of chloride of lead.

Soda has been recommended for keeping a boiler clean, and here I think a great deal of carelessness has been introduced by writers on this subject. One-half of a boiler is in contact with a hot solution of caustic soda, the other half not; the condition of the two parts of the boiler electrically, as regards liability to corrosion, must be too evident to need comment.

The unequally heated parts of a boiler will acquire a difference of potential proportional to the energy of the liquid, and here we have probably an explanation for the increased activity of alkaline solutions in removing scale.

From these considerations it will appear that if we can keep a boiler electro-negative, by an independent source of electrification, to any destructive agency which might arise in the boiler, we might reasonably hope to prolong its life.

EXAMINATION OF CORPSES FOR ALKALOIDS AND METALLIC POISONS.

By Dr. ANTON SEYDA.

(Concluded from p. 235).

As to the objections raised by Otto against this direct determination of arsenic, it is to be remarked that:—(1) A concentration of the strongly hydrochloric diluted liquid may seem altogether superfluous with reference to the sensitiveness of the arsenical reaction. (2) The alleged "brown spots" obtained on the porcelain lid cannot have on the author's process, any disturbing influence, as he on principle refrains from their production.

Independently of the simplicity of execution, this direct determination of arsenic—which was proposed by Marsh himself—cannot be estimated too highly, as we are here secure against the objection of "arseniferous hydrogen sulphide." In the eyes of specialists, this point will, indeed, be of less weight, but the matter is different in actual forensic cases, where an advantageous impression will be produced both on juries and judges by the demonstration of arsenic without the aid of a reagent K_2 sulphuretted hydrogen, which has latterly acquired an evil reputation. The author often effects the detection of arsenic with hydrochloric solutions obtained from parts of organs at once in the direct and indirect manner, and if arsenic is present, the former process has never failed him. In order to be satisfied to what extent the arsenical reaction is interfered with by the presence of nitrates he carried out the following experiment:—

Of a watery hydrochloric solution, containing about 0.75 per cent potassium nitrate and 0.331 per cent arsenious acid, he adds 1 c.c. to parts of organs which

had been stirred up with water and mixed with about 5 grms. potassium chlorate. The chlorination was effected in the manner described above. The filtered hydrochloric solution, free from chlorine, was introduced into the Marsh apparatus, in which hydrogen was evolved from zinc and hydrochloric acid. Fragments of caustic potassa were laid in the calcium chloride tube. After hydrogen had been evolved for eight hours, two arsenical mirrors had been deposited in the reduction tube which corresponded approximately in strength to the quantity of arsenic employed—about 3.0 m.grms. It is to be remarked that a subsequent addition of cane-sugar (free from arsenic) seemed to promote the reaction.

From this experiment it appears that the presence of chlorides, and even of nitrates, does not prevent the formation of gaseous arsenic hydride, at least not to the extent commonly assumed, so long as zinc and hydrochloric acid are present in excess, and the development of hydrogen is allowed to go on for a sufficient time.

In cases of arsenical poisoning such an excess of nitrate as there was used in the above experiment will never occur, since nitrates only occur in the organism in small traces, and, on the other hand, saltpetre, if taken, promptly passes into the urine.

A second supplemental experiment may here be reproduced, which was executed with the following modification:—

In a Marsh apparatus, charged as before with a hydrochloric liquid containing arsenic and saltpetre, hydrogen was generated, and after a time a coating of arsenic appeared in the reduction tube; but as free nitric acid was poured into the flask the escape of hydrogen seemed to cease, as the deposit of arsenic did not become stronger. (The ignition of the gas at the aperture of the reduction tube was not attempted on account of the difficulty of evading the formation of detonating gas within the apparatus). But after some time—about twenty minutes—arsenic again began to deposit in the reduction tube.

From this experiment it would appear that nitrates and free nitric acid in presence of free hydrochloric acid have a different effect upon the formation of gaseous arsenic hydride, so that on the addition of free nitric acid the nascent hydrogen is first consumed in the reduction of the nitric acid, and that afterwards a further reduction of the arsenical compound to gaseous arsenic hydride recommences; but, as free nitric acid can scarcely occur in the examining portions of a corpse, this case has chiefly a theoretical interest. Still, the information to be met with in chemical literature—so far as the author can ascertain—requires an important extension in order to explain all the conditions under which, on the one hand, the formation of gaseous arsenic hydride may be interfered with or hindered, and, on the other, arsenic is reduced from its compounds to a solid hydride or to the free state.

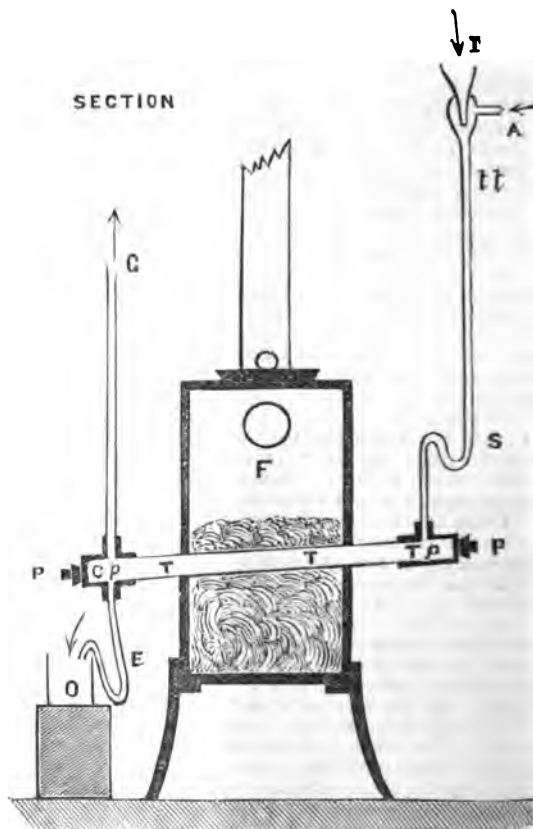
Here the concentration of the solutions and of the acid, its kind, whether sulphuric or hydrochloric, play a great part. It has yet to be decided whether solid arsenic hydride is not converted into the gaseous form in presence of zinc and hydrochloric acid.

Finally, it must be remarked that in examining the organs of a corpse, in poisoning cases in general, only one poison is found, but that we should not overlook how easily in such cases several more or less dangerous substances, inorganic or organic, or both, may have found application (Schweifurt green, mercuric cyanide, chrome yellow, tinctures, &c.). The more or less unconscious state of drunkenness of a person may have been taken advantage of for the purpose of giving him an effective antidote. Portions of a corpse were once sent to the author to be examined for alcohol, but in addition to alcohol arsenic was found in proportion admitting of a quantitative determination. There was consequently room to suspect that arsenic had been administered to the victim whilst in a state of drunkenness.—*Chemiker Zeitung*.

A SIMPLE GAS GENERATOR.

By F. W. ROAM, F.C.S.

In laboratories where the ordinary coal-gas is not obtainable it is often requisite and sometimes necessary to have a supply of a comparatively pure gas at hand. The usual laboratory appliances for producing gas from benzene, methylated spirit, &c., are oftentimes cumbersome, or require constant attention, or are complete failures. It was in order to meet this difficulty to some extent that the author designed the apparatus herein described and illustrated. It consists of an ordinary circular or square cast-iron stove or furnace, *F*, through the body of which passes a short length of $1\frac{1}{4}$ or 2-inch iron pipe, *T*; preferably such as is used for the conveyance of high-pressure steam. This tube is screwed at each end and a



T-piece, *T.P.*, screwed on at the higher end, and at the lower end a "cross-piece" or "four-way socket," *C.P.* At the extreme ends are a couple of "plugs," *P.P.* These, when unscrewed, admit of a rod being pushed through the tube should a stoppage occur, or for cleaning the tube. Into the branch of the top end is fixed a narrow tube, about $\frac{1}{8}$ inch bore, having an S-shape bend towards its lower end, *S*. At the top end it widens out, admitting the nozzle of a funnel, *I*, and the end of a branch tube, *A*. Into the bottom branch of the four-way socket, *C.P.*, is fixed a tube with a syphon bend, *E*, under the end of which is placed a receptacle to catch any surplus oil, *O*. Into the higher branch is screwed a pipe, *G*, to convey the gases produced to the gas-holder.

To start the apparatus, oil (paraffin oil or any fluid hydrocarbon) is allowed to drop from a vessel placed above the funnel, *I*, into the funnel and thence down the

pipe, *tt*, until it commences to overflow at pipe *z*. When this occurs the fire is lighted in the furnace, *r*, and the oil-supply so regulated that each drop of oil carries down with it a small bubble of air. When the tube, *r*, gets hot a form of paraffin gas will be generated and will pass through the pipe, *g*, into the gas-holder. The best form of gas-holder to use is the ordinary sheet-iron dome suspended in a water-tank and counterbalanced by weights attached to cords or chains running over small pulleys. The weight of the holder should be as nearly as possible exactly counterbalanced. If the oil carries along with it too much air, the supply of air may be controlled by means of a piece of rubber tube and a clamp, or a stop-cock. The pressure of the gas is, of course, dependent upon the height of the column of oil in the tubes *tt* and *z*, and therefore, indirectly, upon the length of those tubes. A small apparatus made after this pattern has given very satisfactory results in the author's laboratory, the gas produced being excellent both as an illuminant and for use with Bunsen burners and blast-lamps. It is, of course, also practically free from sulphur compounds, and is suitable for the most delicate work. The cost of the apparatus is next to nothing, and it requires very little attention, while giving a constant and regular supply of gas.

The Laboratory,
Coombe Arsenic Works,
Callington, Cornwall.

A SYSTEM OF CHEMICAL REAGENTS BASED ON THE EQUIVALENTS OF THE ELEMENTS.

By JOS. REDDROP, F.C.S., F.I.C.

The Concentration of Laboratory Reagents.

In a recent number of the *Berichte der Deutsch. Chem. Ges.* (1890, p. 31) R. Blockmann calls attention to a matter which is of the greatest importance in the chemical laboratory, viz., the concentration of the reagents employed. I enclose a copy of the *Chemical Trade Journal* containing an abstract of the above, from which it will be seen that the author proposes the adoption of normal or percentage solutions for general use in chemical analysis.

In the year 1877, I introduced into the new laboratory at Crewe a number of reagents, the strength of which was based on the chemical equivalents. Since that time, their use has extended until it now includes almost all the reagents in the laboratory, and the advantages derived therefrom have been so decided, especially in chemical analysis, that they are now employed in all our investigations. I have, therefore, great pleasure in forwarding a description of the same for publication in the *CHEMICAL NEWS*, to which journal I have been so largely indebted for chemical information.

Chemical Reagents Based on the Equivalents of the Elements.

An equivalent reagent may be defined as one which contains a milligram equivalent of reacting substance in one c.c. of solution, or a gram equivalent in one litre. A solution of this strength is called an equivalent solution, or an equivalent reagent, and is denoted by the symbol *E*, e.g., *E* sodium carbonate represents a solution containing 53 m.grms., = 0.053 gm. in 1 c.c., or 53 grms. in 1 litre. It will be observed that this is not a percentage solution, but one containing parts by weight (m.grms.) of substance, in parts by volume (c.c.) of solution. The strengths of all the reagents are expressed in terms of *E*,* thus the strength of sulphuric acid, sp. gr. 1.84, is approximately 36 *E*; strong nitric acid, sp. gr. 1.42, is

about 16 *E*; and strong hydrochloric acid, sp. gr. 1.16, is about 10 *E*. Many of the reagents employed are made of *E* strength, but in some cases the substance is not sufficiently soluble to make an *E* solution, and consequently some fractional part thereof has to be adopted instead.

Thus we have $\frac{E}{4}$ hydrogen sulphide, $\frac{E}{20}$ calcium oxide,

$\frac{E}{30}$ calcium sulphate, $\frac{E}{600}$ strontium sulphate (test for

barium). The fractional indices may, if preferred, be expressed decimally, thus $\frac{3E}{5}$ or 0.6 *E*. All *E* reagents are

equal in precipitating or quantitative reacting power. For example, if we have a quantity of lead salt in solution which requires 36 c.c. of *E* sulphuric acid to exactly precipitate the lead as sulphate (not allowing for free sulphuric acid in excess), it will require the same number of c.c. of *E* ammonium carbonate to precipitate the lead as carbonate, or of *E* potassium chromate to precipitate the lead as chromate. The same quantity of lead in solution could, however, be precipitated by 1 c.c. of 36 *E* sulphuric acid, or by 7.2 c.c. of 5 *E* ammonium carbonate, but it

would require at least 144 c.c. of $\frac{E}{4}$ hydrogen sulphide

(saturated solution) to precipitate the lead as sulphide.

It may here be pointed out that $\frac{E}{N}$ reagents are not made with the same degree of accuracy as the *N* reagents employed in volumetric analysis. Variations in strength to the extent of from $\frac{1}{100}$ th to $\frac{1}{10}$ th part are not considered inadmissible; they may, consequently, be made in almost the same time as those hitherto employed, and the strength, in terms of *E*, is printed on the label of each bottle, thus—

SULPHURIC ACID. 36 <i>E</i> .
or
SULPHURIC ACID. $36 \frac{H_2SO_4}{2}$.
or
SULPHURIC ACID. 36 <i>E</i> . $E = \frac{H_2SO_4}{2}$.

The accompanying Table includes the reagents to which the equivalent system has already been extended.

Column 1 gives the name of the reagent.

Column 2 the molecular formula of the anhydrous substance.

Column 3 the molecular weight of the anhydrous substance.

Column 4 the equivalent weight of the anhydrous substance.

Column 5 gives the strength of reagent as recommended by Fresenius, "Qual. Analysis," 10th English Edition, first in the terms stated by him, and second, as calculated on the equivalent system. This double column is simply given for comparison.

* *E* being used as the symbol of equivalent or equivalents.

Column .	2.	3.	4	FRESSENIUS'S SYSTEM.		6.	
				Strength of Reagent.		Equivalent System.	
				As stated.	Calculated in equivalents.	Grams. per litre.	Strength.
Sulphuric Acid	H ₂ SO ₄	98	49	Sp. gr. 1·840	36 E	—	36 E
"	"	"	"	1 to 5	6 E	—	5 E
"	"	"	"	—	—	49	E
Nitric Acid	HNO ₃	63	63	—	—	—	24 E—
"	"	"	"	—	—	—	16 E
"	"	"	"	Sp. gr. 1·2	6·16 E	—	5 E
"	"	"	"	—	—	63	E
Hydrochloric Acid ..	HCl	36·5	36·5	—	—	—	10 E
"	"	"	"	Sp. gr. 1·12	7·48 E	—	5 E
"	"	"	"	—	—	36·5	E
Sulphurous Acid	H ₂ SO ₃	82	41	—	—	—	4 E—
"	"	"	"	—	—	—	E
Carbonic Acid	H ₂ CO ₃	62	31	—	—	—	10
Acetic Acid	HC ₂ H ₃ O ₂	60	60	—	—	—	17 E
"	"	"	"	33% of HC ₂ H ₃ O ₂	5·61 E	—	5 E
"	"	"	"	—	—	60	E
Tartaric Acid	H ₂ C ₄ H ₄ O ₆	150	75	—	—	—	5 E
"	"	"	"	—	—	75	E
Citric Acid	H ₃ C ₆ H ₅ O ₇	192	64	—	—	—	5 E
"	"	"	"	—	—	64	E
Oxalic Acid	H ₂ C ₂ O ₄	90	45	—	—	—	3 E
"	"	"	"	—	—	—	2
Hydrofluoric Acid ..	HF	20	20	—	—	—	12 E?
Hydrofluosilicic Acid..	H ₂ SiF ₆	144	72	—	—	—	E
"	"	"	"	—	—	—	E
Hydrogen Sulphide ..	H ₂ S	34	17	Saturated solution	E— 4	—	E— 4
Chlorine Water	Cl ₂	71	35·5	Saturated solution	E— 5	—	E— 5
Bromine	Br ₂	160	80	—	—	—	37 E
"	"	"	"	—	—	—	E
Bromine Water	"	"	"	—	—	—	2
Hydrogen Peroxide ..	H ₂ O ₂	34	17	—	—	—	4 E—
"	"	"	"	—	—	—	2 E—
Potassium Hydrate ..	KHO	56	56	—	—	—	5 E
"	"	"	"	—	—	56	E
Sodium Hydrate ..	NaHO	40	40	Sp. gr. 1·13 = 9% Na ₂ O	3·28 E	—	5 E
"	"	"	"	—	—	40	E
Ammonium Hydrate..	AmHO	35	35	Sp. gr. 0·96 = 10% NH ₃	5·54 E	—	20 E—
"	"	"	"	—	—	—	5 E
"	"	"	"	—	—	35	E
Barium Oxide	BaO	153	76·5	BaH ₂ O ₂ . 8Aq. 1 to 20	E— 3·15	—	E— 3
Calcium Oxide	CaO	56	28	Saturated solution	E— 20	—	E— 20
Ammonium Sulphide .	Am ₂ S	68	34	10% NH ₃	5·54 E?	—	5 E
"	"	"	"	—	—	34	E
Sodium Sulphide ..	Na ₂ S	78	39	9% Na ₂ O	3·28 E	—	5 E
"	"	"	"	—	—	39	E
Potassium Cyanide ..	KCy	65	65	—	—	65	E
Potassium Sulphate ..	K ₂ SO ₄	174	87	1 to 12	0·96 E	—	E
Potassium Iodide ..	KI	166	166	—	—	166	E
"	"	"	"	—	—	—	E
"	"	"	"	—	—	—	5
Potassium Chromate .	K ₂ CrO ₄	194·5	97·25	—	—	97·25	E
Potassium Metanti- moniate	KSbO ₃	209	209	Saturated solution	E— 68	3·07	E— 68
Potassium Ferrocyanide	K ₄ FeCy ₆	368	92	1 to 12	0·79 E	92	E
Potassium Ferricyanide	K ₃ FeCy ₆	658	109·7	—	—	109·7	E
Potassium Sulphocyanate	KCyS	97	97	1 to 10	1·03 E	97	E

Symbol of substance taken.	Method of Preparing Reagent.	Strength of Reagent as found by trial.
—	Sulphuric acid, sp. gr. 1.8427 at 15.5° C. Note (1).	36 E
—	Sulphuric acid diluted to sp. gr. 1.1527 at 15.5°. Note (2).	5 E
—	200 c.c. of 5 E sulphuric acid diluted to 1 litre.	E
—	Nitric acid sp. g. 1.50. Note (3).	22.8 E
—	Nitric acid sp. gr. 1.4268 at 15.5° C. Note (4).	16 E
—	Nitric acid diluted to sp. gr. 1.1656 at 15.5° C. Note (2).	5 E
—	200 c.c. of 5 E nitric acid diluted to 1 litre.	E
—	Hydrochloric acid sp. gr. 1.1611 at 15.5° C. Note (5).	10 E
—	Hydrochloric acid diluted to sp. gr. 1.0843 at 15.5° C. Note (2).	5 E
—	200 c.c. of 5 E hydrochloric acid diluted to 1 litre.	E
—	Water at 15.5° C. saturated with sulphur dioxide (sp. gr. 1.052).	3.7 E
—	Water at 15.5° C. saturated with carbon dioxide. Note (6).	—
—	Acetic acid solid at 10° C. Note (7).	16.9 E
—	294 c.c. of 17 E acetic acid diluted to 1 litre. Note (2).	5 E
—	200 c.c. of 5 E acetic acid diluted to 1 litre.	E
H ₂ C ₄ H ₄ O ₆	375 grm. dissolved and diluted to 1 litre.	5 E
H ₃ C ₆ H ₅ O ₇ , 4Aq]	75 " " "	E
"	350 " " "	5 E
"	70 " " "	E
H ₂ C ₄ O ₄ , 2Aq	94.5 " " Note (8).	3 E
—	Hydrofluoric acid, sp. gr. 1.15.	2
—	Water at 15.5° C. saturated with hydrogen sulphide.	12.9 E
—	Water at 15.5° C. saturated with chlorine.	24 E
—	Pure liquid bromine. Note (9).	100
—	Water at 15.5° C. saturated with bromine.	19 E
—	Hydrogen peroxide, 20 volume solution. Note (10).	100
—	" " " " " " Note (11).	—
KHO	280 grms. dissolved and diluted to 1 litre. Note (12).	—
NaHO	56 " " " " " " Note (13).	—
—	200 " " " " " " Note (13).	—
—	40 " " " " " " Note (13).	—
—	Ammonium hydrate sp. gr. 0.880. Note (14).	18.9 E
—	Ammonium hydrate diluted to sp. gr. 0.9643 at 15.5° C. Note (2).	5 E
—	200 c.c. of 5 E ammonium hydrate diluted to 1 litre.	E
BaH ₂ O ₂ , 8Aq	52.5 grm. dissolved and diluted to 1 litre. Note (15).	—
—	Water at 15.5° C. saturated with calcium hydrate.	97 E
—	Saturate 600 c.c. of 5 E ammonium hydrate with H ₂ S in a corked flask, and then add 400 c.c. of 5 E ammonium hydrate.	2000
—	200 c.c. of 5 E ammonium sulphide diluted to 1 litre.	5 E
—	Dissolve 200 grms. of sodium hydrate in 800 c.c. water, saturate one-half with H ₂ S, then add the other half and dilute to 1 litre.	E
—	200 c.c. of 5 E sodium sulphide diluted to 1 litre.	5 E
KCy	65 grms. crystal dissolved and diluted to 1 litre.	E
K ₂ SO ₄	87 grms. dissolved and diluted to 1 litre.	—
KI	166 " " " " " " Note (18).	E
"	33.2 " " " " " " Note (18).	E
K ₂ CrO ₄	97.25 " " " " " "	5
K ₂ Sb ₂ O ₆ , 7Aq	Saturated solution at 15.5° C.	E
K ₄ FeCy ₆ , 3Aq	105.5 grm. dissolved and diluted to 1 litre.	—
K ₆ Fe ₂ Cy ₁₂	109.7 " " " " " "	E
KCyS	97 " " " " " "	E

Column 6 gives the strength of reagent recommended on the equivalent system, first in grms. per litre, and second in terms of E.

Column 7 gives the chemical formula of the substances used, and the methods by which the reagents are prepared of sufficient accuracy for general use.

Column 8 gives the strength of reagent as determined by trial after being prepared by the method given.

Several notes are also appended, to which the reader should refer for further information.

NOTES TO TABLE I.

- (1) Sulphuric acid, sp. gr. 1.842, containing 98.6 per cent, by calculation gives 37.07 E.

Sulphuric acid, sp. gr. 1.84, as supplied, two samples titrated gave 36.6 E and 36.8 E.

- (2) I usually make 5 litres of 5 E acid at a time and adjust the strength by titrating 2 c.c. with standard N sodium hydrate. This can be done more quickly than by using the hydrometer, owing to changes of temperature on dilution. 5 E ammonium hydrate may be made in a similar manner. These 5 E reagents may also be made by simply diluting the concentrated ones to the right degree.

- (3) Nitric acid, sp. gr. 1.50, containing nitrous acid, titrated, gave 22.8 E.

- (4) Nitric acid, sp. gr. 1.424, containing 70.2 per cent, by calculation gives 15.87 E.

Nitric acid, sp. gr. 1.42, as supplied, two samples titrated gave 16.05 E and 16.6 E.

- (5) Hydrochloric acid, sp. gr. 1.160, containing 31.73 per cent by calculation, gives 10.08 E.

Hydrochloric acid, sp. gr. 1.16, as supplied, two samples titrated gave 10.36 E and 10.32 E.

- (6) Carbonic acid. Water at 15° C. dissolves 1.0020 vols.

of CO₂; this, by calculation, gives $\frac{100 E}{111.4}$.

- (7) Acetic acid, anhydrous, sp. gr. 1.0635, containing 100 per cent, by calculation gives 17.7 E.

Acetic acid, sp. gr. 1.0598, solid at 50° F., as supplied, titrated, gave 16.9 E.

- (8) Oxalic acid. A $\frac{3 E}{2}$ solution does not crystallise out at 15° C., but does so at 10° C.

- (9) Bromine, sp. gr. 2.966, by calculation gives 37.08 E.

- (10) Hydrogen peroxide, 20 volumes, by calculation gives 3.6 E.

- (11) Hydrogen peroxide, 10 volumes, by calculation gives 1.8 E.

- (12) Potassium hydrate, about one-tenth more than the quantity given in the table is required, owing to most samples containing water.

- (13) Sodium hydrate prepared from sodium is employed.

- (14) Ammonium hydrate, sp. gr. 0.88, containing 38 per cent, by calculation gives 19.7 E.

Ammonium hydrate, sp. gr. 0.88, as supplied, three samples titrated gave 18.0 E, 16.2 E, and 18.9 E.

- (15) Barium hydrate. The strength of a saturated solution varies considerably with the temperature.

- (16) Ammonium oxalate. A stronger solution than $\frac{3 E}{5}$ crystallises out at the ordinary temperature.

- (17) Barium nitrate is not sufficiently soluble to make an E solution.

- (18) Where reagents are expensive an $\frac{E}{5}$ or $\frac{E}{10}$ solution may be made for qualitative tests.

It will be seen from the Table that a large number of the reagents are made of E strength. Experience, however, has shown that there are cases in which it is necessary to employ certain reagents, and especially the acids, stronger than this; consequently, a number of 5 E

reagents have been introduced, 5 being a convenient figure for calculations on the decimal system. These are more accurately made, and keep more constant in strength than the concentrated reagents, which are liable to a variation of about one equivalent.

About three-fourths of the reagents given in the Table may be kept in well-stoppered bottles for a considerable time without appreciable change. In the few remaining cases where the variation in strength is considerable, the unwelcome fact is expressed in column 6 of the preceding Table and on the reagent bottles in the following manner:—

Where it is known that the reagent has been made the standard strength, but becomes weaker on keeping, it may be expressed by the sign — placed after the symbol E, thus:— 4 E— Sulphurous Acid. If, on the other hand, there is an increase of strength, as in the case of the acid solution of stannous chloride kept in contact with metallic tin, it may be expressed thus:— E+ Stannous Chloride. The analyst is thus forewarned as to any irregularity which may occur in the strength of such reagents.

The practical application of these multiple and fractional equivalents is well illustrated by the chlorine and bromine reagents given in the table. Pure liquid bromine is shown as 37 E; a saturated solution of bromine in

water as $\frac{E}{2}$; and a saturated solution of chlorine in water $\frac{E}{5}$. Now if we know that 1 c.c. of liquid bromine (37 E)

is required to effect a definite amount of oxidation in a solution, we see at a glance by means of these equivalents that it would require 74 c.c. of $\frac{E}{2}$ bromine-water or

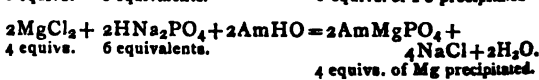
185 c.c. of $\frac{E}{5}$ chlorine-water to effect the same quantitative result.

It may here be pointed out that a few reagents require a double index of their strength, e.g., E or $\frac{2 E}{3}$ hydrogen

disodium phosphate.* This reagent behaves as an E solution if employed to precipitate iron as phosphate,

but only as $\frac{2 E}{3}$ when employed to precipitate magnesium

as ammonium magnesium phosphate owing to ammonium taking part in the reaction. A reference to the chemical equations representing the reactions will illustrate this:—



(To be continued).

TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES.†

By F. A. GOOCH and F. W. MAR.

(Continued from p. 225).

THE next point to be considered was the proper mode of breaking up hydriodic acid and volatilising the iodine thus set free, while leaving the hydrochloric acid fixed.

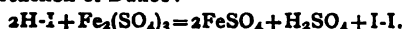
* On this account the second or third label previously given is preferred.

† Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., April, 1890.

Series H.

Taken H ₂ SO ₄ [1:1]. Grms.	Taken iron alum. Grms.	Taken HNO ₃ sp. gr. 1.40. C.m.s.	Taken KCl+HCl. Grm.	Initial volume. C.m.s.	Final volume. C.m.s.	Time in minutes.	Found AgCl. Grm.	Loss of HCl. Grm.
—	—	1	1 0.4888	200	100	30	0.0006	0.0002
—	—	1	1 0.4888	100	50	14	0.0010	0.0003
—	—	1	1 0.4888	50	15	10	0.0049	0.0012
10	—	1	1 0.4888	200	100	27	0.0031	0.0008
10	—	1	1 0.4888	100	50	16	0.0116	0.0029
10	5	0.1	1 0.4888	400	300	24	0.0004	0.0001
10	5	0.3	1 0.4888	400	300	30	0.0004	0.0001
10	5	0.5	1 0.4888	400	300	30	0.0004	0.0001
10	5	1	1 0.4888	400	300	27	0.0010	0.0003
10	5	1	1 0.4888	300	200	33	0.0007	0.0002
10	5	1	1 0.4888	200	100	30	0.0025	0.0006
10	5	1	1 0.4888	100	50	15	0.0090	0.0023
10	5	2	1 0.4888	400	300	25	0.0010	0.0003
10	5	3	1 0.4888	400	300	25	0.0010	0.0003
10	5	4	1 0.4888	400	300	30	0.0009	0.0002
10	5	5	1 0.4888	400	300	30	0.0007	0.0002
10	5	10	1 0.4888	400	300	30	0.0018	0.0005

The use of dihydrogen potassium arseniate, which has been utilised to liberate iodine according to a method recently developed in this laboratory,* is precluded by the necessarily high degree of dilution of the solution employed. The first trials were made, therefore, with ferric alum to act as the oxidising agent according to the well-known reaction of Duflos:—



We found by experiment that from a volume of 300 c.m.³ containing 10 c.m.³ of sulphuric acid [1:1], 5 grms. of ferric alum, and 0.005 grm. of potassium iodide, every trace of iodine had disappeared so completely after five minutes boiling that nitrous acid and chloroform collected no colour in the cooled liquid. It transpired, however, that when the amount of potassium iodide was increased to 1 grm., iodine was found in considerable amount after boiling for an hour with occasional replacing of the water evaporated, so that the volume should not decrease much below 300 c.m.³. The failure of the iron alum to expel the iodine is not attributable to a deficiency in amount; for the 5 grms. present were capable of decomposing more than a grm. and a half of potassium iodide were the full effect theoretically possible attained. Furthermore, special tests, in which the amount of ferric alum was increased, developed the fact that the increase was but little helpful. The apparent explanation of the phenomenon is that here, as in the liberation of iodine by means of dihydrogen potassium arseniate, there occurs a time in the course of action when for a given degree of dilution an equilibrium is established between the tendency of the oxidiser to oxidise and that of the reduced residue to reverse the action. The obvious modes of securing completed action are the concentrating of the liquid and the reinforcing of the oxidiser. Application of the former is precluded by the danger of volatilising hydrochloric acid; the simplest mode of realising the latter—and, as the result proved, a feasible one—is the re-oxidation of the reduced ferrous sulphate by means of nitric acid.

When a sufficient amount of nitric acid is added to restore the iron to the ferric state, the boiling of the solution resulted in the complete liberation of the iodine. In dilute solutions the amount of nitric acid necessary to oxidise a fixed quantity of ferrous salt is greater than in concentrated solutions. Thus, while 0.1 c.m.³ of strong nitric acid should be more than enough to re-oxidise the iron reduced by 1 grm. of potassium iodide when the full oxidising action is brought out, we found it necessary to add to the dilute solutions with which we worked about 2 c.m.³ of the acid to complete the action satisfactorily. Incidentally, we found that nitric acid by itself—that is,

without the presence of the iron salt—is not effective in liberating the iodine; for, the successive addition of portions of 1 c.m.³ of nitric acid to a solution containing 10 c.m.³ of sulphuric acid [1:1], and 1 grm. of potassium iodide in a total volume of 400 c.m.³ until the amount of nitric acid reached 5 c.m.³, the liquid boiling all the time, liberating but little iodine, while the addition at this point of 2.5 grms. of ferric alum determined the evolution of iodine in dense fumes.

The addition of 2 c.m.³, or at the most 3 c.m.³, of strong nitric acid to solutions constituted as has been described, proved to be sufficient to liberate the entire amount of iodine present. The question as to whether the hydrochloric acid is affected by the addition of so much nitric acid was settled in the experiments of the following series. In these determinations a little sulphurous acid was added to each distillate to insure the complete precipitation of the chlorine by silver nitrate, and sufficient nitric acid was added to re-dissolve the silver sulphite thrown down also at first.

It appears in these results that the ferric salt has no perceptible influence upon the hydrochloric acid, and that the presence of nitric acid within reasonable limits does not sensibly increase the loss of hydrochloric acid which takes place under conditions otherwise similar, strong nitric acid to the amount of 5 c.m.³ in a total volume of 300 c.m.³ producing no apparent increment of loss from half a grm. of hydrochloric acid. The nitric acid itself passes easily into the distillate. That the influence of the sulphuric acid is important is again demonstrated in the experiments in which 1 c.m.³ of nitric acid and 1 grm. of potassium chloride were distilled in the one case with, and in the other without, the addition of sulphuric acid.

In the indication of these and previous experiments we found warrant for the prosecution of the quantitative tests of the following series:—

Weighed portions of a standard solution of potassium chloride (whose value was determined by precipitating with silver nitrate with the usual precautions, collecting in a perforated crucible upon asbestos felt the silver chloride found, and drying and weighing it) were transferred to Erlenmeyer flasks of 500 c.m.³ capacity, water was added with 10 c.m.³ of sulphuric acid [1:1], 2 grms. of ferric sulphate (either in the form of iron alum or an equivalent amount of ferrous sulphate oxidised in concentrated solution with a sufficiency (0.3 c.m.³) of nitric acid) and 1 grm. of potassium iodide were introduced, the whole volume was brought to 400 c.m.³, and the liquid was boiled with the addition of nitric acid as indicated in the Table, 1 c.m.³ being added after it appeared that all iodine had been expelled.

(To be continued).

* Gooch and Browning, *American Journal of Science*, vol. xxxix., p. 288.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London
Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, May 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, 164 were found to be clear, bright, and well filtered, four being recorded as "very slightly turbid."

The character of the water furnished to the Metropolis during the month of April was not found to differ appreciably from that observed during the previous month. Thus, taking the Thames-derived water for comparison, the mean proportion of organic carbon present in the supply for April was found to be 0.148 part in 100,000 parts of the water, as against a mean of 0.154 part in the supply of the previous month. Again, the mean amount of oxygen absorbed in the oxidation of the organic matter present in a gallon of the April water was found to be 0.039 grain, as against a mean of 0.041 grain for the water of the previous month; while the fraction indicating the mean degree of colour-tint of the April water was $\frac{1}{11}$, as against the fraction $\frac{1}{10}$ for the previous month; all these differences being insignificant, but the last named being in the opposite direction to the other two.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

SUMMARY OF USEFUL TESTS WITH
THE BLOWPIPE.*

By A. J. MOSES.
(Continued from p. 234).

NICKEL, Ni.

On Coal.—R. F., the oxide becomes magnetic.

With Borax.—O. F., violet hot, pale reddish brown cold.

R. F., cloudy and finally clear and colourless.

With S. Ph.—O. F., red hot, yellow cold.

R. F., red hot, yellow cold. On coal with tin becomes colourless.

Interfering Elements.

General Method.—Saturate two or three borax beads with roasted substance, and treat on coal with a strong R. F. If a visible button results, separate it from the borax and treat with S. Ph. in the O. F., replacing the S. Ph. when a colour is obtained.

If no visible button results, add either a small gold button or a few grains of test lead. Continue the reduction, and—

With Gold.—Treat the gold alloy on coal with S. Ph. in strong O. F.

With Lead.—Scorify button with boracic acid to small size, complete the removal of lead by O. F. on coal, and treat residual button with S. Ph. in O. F.

Arsenic.—Roast thoroughly, treat with borax in R. F. as long as it shows colour, treat residual button with S. Ph. in O. F.

Alloys.—Roast and melt with frequently changed borax in R. F., adding a little lead if infusible. When the borax is no longer coloured, treat residual button with S. Ph. in O. F.

NITRIC ACID, HNO₃.

In Matraass with KHSO₄ or in Closed Tube with Litharge.—Brown fumes with characteristic odour. The fumes will turn ferrous sulphate paper brown.

PHOSPHORUS, P.

Flame.—Greenish blue, momentary. Improved by conc. H₂SO₄.

In Closed Tube with Dry Soda and Magnesium.—The soda and substance are mixed in equal parts and dried, and made to cover the magnesium. Upon strongly heating, there will be a vivid incandescence, and the resulting mass, crushed and moistened, will yield the odour of phosphoretted hydrogen.

POTASSIUM, K.

Flame.—Violet, except borates and phosphates.

Interfering Elements.

Sodium.—(a) The flame, through blue glass, will be violet or blue. (b) A bead of borax and a little boracic acid, made brown by nickel, will become blue on addition of a potassium compound.

Lithium.—The flame, through green glass, will be bluish green.

SELENIUM, Se.

On Coal, R. F.—Disagreeable horse-radish odour, brown fumes, and a volatile steel-grey coat with a red border.

In Open Tube.—Steel-grey sublimate, with red border, sometimes white crystals.

In Closed Tube.—Dark red sublimate and horse-radish odour.

Flame.—Azure-blue.

On Coal with Soda.—Thoroughly fuse in R. F., place on bright silver, moisten, crush, and let stand. The silver will be blackened.

SILICON, Si.

On Coal with Soda.—With its own volume of soda dissolves with effervescence to a clear bead. With more soda the bead is opaque.

With Borax.—Clear and colourless.

With S. Ph.—Insoluble. The test made upon a small fragment will usually show a translucent mass of undissolved matter of the shape of the original fragment.

When not decomposed by S. Ph., dissolve in borax nearly to saturation, add S. Ph., and re-heat for a moment. The bead will become milky or opaque-white.

SILVER, Ag.

On Coal.—Reduction to malleable white metal.

With Borax or S. Ph.—O. F., opalescent.

Cupellation.—Fuse on coal with 1 vol. of borax glass and 1 to 2 vols. of test lead in R. F. for about tw

* From the *School of Mines Quarterly*, vol. xi., No. 1.

minutes. Remove button and scorify it in R. F. with fresh borax, then place button on cupel and blow O. F. across it, using as strong blast and as little flame as are consistent with keeping button melted.

If the litharge is dark, or if the button freezes before brightening, or if it brightens but is not spherical, re-scorify it on coal with borax, add more test lead, and again cupel until there remains only a white spherical button of silver.

SODIUM, Na.

Flame.—Strong reddish yellow.

STRONTIUM, Sr.

On Coal with Soda.—Insoluble, absorbed by the coal.

Flame.—Intense crimson, improved by moistening with HCl.

With Borax or S. Ph.—Clear and colourless; can be flamed opaque.

Interfering Elements.

Barium.—The red flame may show upon first introduction of the sample into the flame, but it is afterwards turned brownish yellow.

Lithium.—Fuse with baric chloride, by which the lithium flame is unchanged.

(To be continued).

CORRESPONDENCE.

THE VOLUMETRIC ANALYSIS OF COPPER.

To the Editor of the Chemical News.

SIR,—As regards the use of a sodium carbonate solution of copper in titrating with KCy, it has been objected—

1. That sodium carbonate does not dissolve, but precipitates copper.

2. That a large quantity is necessary to effect solution.

3. That the quantity of sodium carbonate in the solution affects the amount of KCy used.

As regards 1, it is evident either that the experiment was not tried, or that the solution did not contain the free nitric acid stated in the previous note to be necessary. Sodium bicarbonate, however, contrary to what might be expected, does not give a solution under these circumstances.

In reference to 2 the same remarks apply, as on making the experiment it will be found that 20 to 30 c.c. is amply sufficient for any ordinary analysis, and this is but a few c.c. above that required to neutralise the excess of acid necessarily used in dissolving the copper sulphide. Moreover, the increased accuracy of the method permits the use of much smaller quantities of ore in assaying.

If the sodium carbonate is added, first to the copper and then the nitric acid (not sufficient, of course, to render the solution acid) a much larger quantity of sodium carbonate will be found necessary. In actual working, however, this order will never be followed.

To 3 I may say that no such disturbance has been noticed. To one of two copper solutions of equal strength and volume, and containing equal quantities of free nitro-sulphuric acid, was added 20 c.c. of sodium carbonate solution (saturated). This was just sufficient to redissolve the precipitated copper. To the other was added 250 c.c. of the same solution of sodium carbonate. On titration the amount of KCy used for each was identical.

It is true that when NaOH (or Na_2CO_3 in absence of free acid) is used to render the copper solution alkaline the amount of KCy used varies greatly: this for the following reason. When a small excess of NaOH is added a very unstable salt separates out, having a large molecular weight. As more alkali is added the precipitate becomes more simple, more stable, and therefore less

readily acted upon by the KCy. When, however, the alkali added forms a solution the case is not analogous.

The above reaction can also be made use of in the volumetric estimation of nickel.

REGINALD A. FESSENDEN,

Edison Laboratory, Orange, N.J.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 18, May 5, 1890.

Combustion—Heat of the Principal Nitrogenous Compounds contained in Living Beings and its Part in the Production of Animal Heat.—MM. Berthelot and André.—The authors have operated upon purified egg-albumen, purified blood fibrine, muscular flesh, hæmoglobine (obtained from a horse), caseine (from milk), osseine, purified chondrine, vitelline, yolk of egg, vegetable fibrine, crude gluten, isinglass, fibroine, wool, chitine, and tunicine. Under each was determined the composition of the specimen, the heat of combustion (referred to 1 grm. of carbon), the formation-heat from the elements, and the heat of combustion with formation of urea. The mean value of the combustion-heat for the albumenoid bodies capable of playing an alimentary part is, per grm., 5691 cal., and for a weight of the substance containing 1 grm. of carbon, 10,870 cal. The loss of heat due to the elimination of nitrogen in the form of urea is about one-sixth of the total combustion-heat of the substances.

Preparation and Properties of Carbon Tetrafluoride.—H. Moissan.—Of five different methods of preparing this compound the author gives the preference to the one which depends on the action of silver fluoride upon carbon tetrachloride. The operation must be conducted in a tube of brass. The tetrafluoride has the density 3.09 (theoretically 3.03). It liquifies at -15° under the ordinary pressure and 20° under a pressure of 4 atmospheres. It is sparingly soluble in water but dissolves freely in ether and especially in absolute alcohol. If heated in contact with glass it yields carbonic acid and silicon fluoride. If heated with sodium it is absorbed entirely, giving a deposit of carbon and sodium fluoride.

Reduction of Nitric Acid to Ammonia and a Method of Determining this Acid.—E. Boyer.—The solutions of nitrate to be reduced should contain at most 5 grms. of a pure nitrate in 100 c.c. The author takes a test-tube closed at one end, 0.30 metre long and 0.022 in diameter with a spout at its upper end, and introduces 5 grms. of zinc of the size of a pea, a quantity sufficient to cover the bottom of the tube. He takes, then, 10 c.c. of the solution, corresponding to 0.5 grm. of nitrate, and introduces it into the tube, keeping the lower end of the pipette near the bottom of the tube, so as not to splash the sides. He then introduces 5 c.c. of hydrochloric acid of sp. gr. 1.19, letting it run down the sides of the tube, and agitates it circularly. The hydrogen is given off at all points of the bottom of the tube and traverses the solution uniformly from bottom to top. When the escape of hydrogen has nearly ceased he adds again 5 c.c. of hydrochloric acid, which completes the reduction of the nitric acid to ammonia. In ten minutes the reduction is complete. The liquid contained in the tube then consists of a mixture of hydrochloric acid, ammonia, zinc chloride, and undissolved zinc. This mixture is distilled with caustic magnesia in Schloësing's apparatus, and the ammonia is collected and determined in the usual manner.

Molecular Refractive Powers of Salts in Solution.—E. Doumer.—This memoir cannot be usefully abridged.

Action of Oxygenated Water upon Permanganic Acid and the Permanganates.—A. Gorgeu.—Under the influence of hydrogen peroxide a solution of permanganic acid is gradually decolourised, whilst heat and oxygen are evolved and the peroxide is deposited. In contact with oxygenated water the alkaline permanganates are gradually decolourised, whilst there is precipitated a peroxide containing a large proportion of alkali.

Amethylcamphophenolsulphone and a Tetranitro Colouring-matter derived from the Same.—P. Cazeneuve.—The amethylcamphophenolsulphone yields the colouring-matter on treatment with fuming nitric acid. It dyes splendid yellows and oranges on wool and silk without a mordant.

Archives Néerlandaises des Sciences Exactes et Naturelles.
Vol. xxiv., Part 1.

Molecular Theory of a Substance Composed of two different Matters.—J. D. van der Walls.—An elaborate mathematical paper not susceptible of useful abstraction.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 2.

Remarks on a Discourse by Mr. W. Crookes relating to the History of the Rare Earths.—Lecoq de Boisbaudran.—Already noticed.

Preparation of Capryl Chloride by Means of Caprylic Alcohol saturated with Hydrochloric Acid.—H. Malbot.—The alcohol above named is heated in a closed vessel with a large proportion of very strong hydrochloric acid. The etherification is very rapid and almost quantitative.

No. 3.

Combinations of Hydroxylamine with Metallic Chlorides.—L. Crismer.—The author has formed the bi-hydroxylamine compounds of zinc chloride, cadmium chloride, and barium chloride. Experiments with the corresponding salts of calcium, magnesium, iron, and cobalt gave no decided results.

Presence of Boric Acid in Plants.—E. Bechi.—The author denies the novelty of the observations of M. von Lippmann and M. Crampton on this subject.

A New Class of Diacetones.—A. Béhal and V. Auger.—Not adapted for useful abstraction.

MEETINGS FOR THE WEEK.

TUESDAY, 27th.—Royal Institution, 3. "The Natural History of Society," by Andrew Lang.
Royal Medical and Chirurgical, 8.30.
WEDNESDAY, 28th.—Society of Arts, 8.
THURSDAY, 29th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
FRIDAY, 30th.—Royal Institution, 9. "Astronomical Telescopes," by A. A. Common, F.R.S., Treas. R.A.S.
SATURDAY, 31st.—Royal Institution, 3. "The Ballad Music of the West of England" (with musical illustrations), by Rev. S. Baring-Gould, M.A.

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AND
JOURNAL OF PHYSICAL SCIENCE.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1592.

NOTE ON THE ESTIMATION OF RESIN BY GLADDING'S METHOD.

By J. A. WILSON.

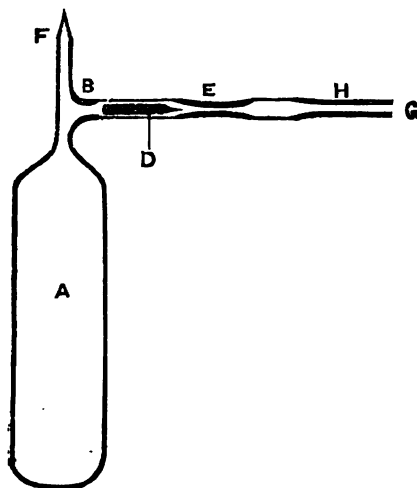
IN estimating resin in oils, fats, or soaps, it is very important that every trace of neutral fat be saponified. If this be not the case, it finds its way into the resultant ethereal layer, and, of course, vitiates the results to the extent named. In soaps where the cold, or semi-cold, process is used in their fabrication, it is especially necessary to guard against the above source of error.

ARRANGEMENT FOR SEALING TUBES UNDER PRESSURE.

By A. RICHARDSON.

IN experimenting with gases under pressure I have found it necessary to seal tubes hermetically after gases have been admitted under pressure. In order to do this the following arrangement was employed with complete success:—

The experimental tube, A, is joined to a T-piece, B, the lateral limb of which is constricted as shown in the figure; a glass plug, D, is ground into the tube at E, and



serves the purpose of a valve opening inwards. When gas under pressure is allowed to enter the tube at G the valve opens, but, on removing the pressure from without, it at once closes; the escape of gas from A is thus prevented, and the tube may be sealed before the blowpipe at H. When the tube contains a liquid the plug should be moistened with it; this will prevent the escape of gas whilst the tube is being sealed, even though the plug does not fit very accurately; in the absence of any liquid greater care in grinding the plug is required. The tube, F, serves for the admission of liquid into the experimental

tube in the first instance; it is then closed, and at the end of the experiment it is opened and the contents of the tube removed. The rest of the apparatus is thus kept intact, and may be used repeatedly, especially if the tube at H is fairly long.

University College, Bristol,
May 17, 1890.

MANURE DRYERS.

By VINCENT EDWARDS, F.C.S.

(Concluded from p. 232).

IT would not be possible for me to give particulars of all substances used for the above purpose, so I merely select one or two which I know to be used to a considerable extent. I certainly think the results of my experiments go to prove that a careful analysis of all substances is necessary unless the quality of the manure is of no importance. I understand that soot is used to mix not only with superphosphates but special manures; the nitrogen and ammonia contained in it, of course, making it of particular value for the latter. I may here mention that consumers ought to know the ingredients of this class of fertilisers, as I have found in some cases the black colour covers a multitude of sins, most of them of omission. It is very doubtful, however, if the ammonia is of sufficient value to counterbalance the injury wrought by iron and alumina in some specimens, though they may not be the only cause of reduction of soluble phosphate. I think there is some obscure action at work which is not very well understood at present; an action which may be more mechanical than chemical.

EXPERIMENT No. 2.—*Soot*.—I procured a quantity from a local dealer who collects it largely, and which appears to contain a great variety of substances, brick dust, broken glass, stones, and other strange matters, which, if not rich and rare, are certainly wonderful results from the combustion of coal. They, of course, reduce the quantity of ammonia, which varies from 1 to 4 per cent. I found on testing it contained, soluble in HCl, 8.0 per cent Fe_2O_3 , 0.5 per cent Al_2O_3 . I made with this a mixture containing 80 per cent of the superphosphate and 20 per cent of the soot; this is rather more than would be added to dry superphosphate, but the iron being less than in the last experiment I increased the amount. I allowed this mixture to stand ten days, being anxious to conclude these experiments, though that is hardly time enough. On testing the mixture the result was 19.75 per cent of soluble phosphate. This shows a fall of 7.97 per cent instead of 5.544 per cent due to the addition of inert matter, or 2.426 per cent loss in ten days, owing to conversion of monocalcium phosphate into phosphate of iron and alumina; a considerable reduction of strength which is no doubt continuously at work, and which reduced special manures to the ridiculous figure of 5 or 6 per cent soluble phosphate.

EXPERIMENT No. 3.—*Flue Dust*.—This is a somewhat vague title for a number of substances which I am led to believe are added to manures. They are of various composition, according to H. A. Smith; some kinds of flue dust contain large quantities of arsenic, which is highly undesirable. I have analysed dust from different parts of vitriol plant, and find in all a considerable quantity of soluble iron together with a siliceous compound, insoluble in acids, which is not so injurious. I found in a recent sample 14.5 per cent soluble Fe_2O_3 , and made the following experiment with it, though I consider it better than some kinds of dust. I added 10 per cent of dust to the superphosphate and allowed the mixture to stand for ten days. On analysis, I found 21.85 per cent soluble phosphate; this shows a fall of 5.87 per cent instead of 2.772 per cent, a loss of 3.098 per cent in ten days, a loss which would become greater after a time as the iron is in a less

soluble state owing to the absence of water of hydration.

EXPERIMENT No. 4.—Gypsum.—I thought well to try an experiment with a good quality of gypsum, and obtained a quantity which came from a north of England firm; It was of a rose colour and very dry. On testing, I found it contained 1·5 per cent of Fe_2O_3 and Al_2O_3 , though there was more iron in a combined state with silica; this is not of much importance. I may note here that calcining gypsum, though it would render some iron less soluble, would drive off CO_2 from any carbonate of lime present, when the oxide left would reduce the soluble phosphate. I made a mixture of 10 per cent gypsum and 90 per cent superphosphate, which I allowed to remain for ten days; it did not dry the manure as well as the cinders. On testing, I found 24·7 per cent soluble phosphate, which is satisfactory, being a loss of only 0·3 per cent. This would have been otherwise with some bad kinds of gypsum. In all cases an analysis is desirable.

EXPERIMENT No. 5.—To prove that the reduction is due to soluble iron and alumina, I made a mixture of superphosphate with 10 per cent crystallised sulphate of iron; not having the pure at hand, I employed the commercial salt, which, however, does not make much difference. On analysis, I found but 11·4 per cent soluble phosphate, a loss of 13·548 per cent, which had been reduced to basic phosphate of iron.

I notice in Dr. Griffiths's recent book that a patent manure, "ferrous superphosphate," was not a success, due, no doubt to the precipitation of the phosphate in a very insoluble condition by the sulphate of iron. Of course, I am aware that the proportions of any of the mixings I have given are not as they might be made by a manufacturer, but I think I have shown enough to prove how injurious is the present method of adding anything almost to manures, and without knowing what it contains. Some substances are no doubt valuable for dressing and composts, but very hurtful to manure during manufacture. The use of Belgium phosphate and good gypsum as dryers would be the best plan and avoid much waste of good manure. The price would have to be raised by all makers, along with the quality, but this would enable farmers to use less, and thus save railway rates on stuff that is always at hand; both sellers and buyers would gain by improvement in quality and manufacture.

A SYSTEM OF CHEMICAL REAGENTS BASED ON THE EQUIVALENTS OF THE ELEMENTS.

By JOS. REDDROP, F.C.S., F.I.C.

(Concluded from p. 250).

Advantages of the System.

HAVING thus briefly described the proposed system of reagents, we will proceed to notice some of the advantages attending its employment in practical and analytical chemistry:—

1. It affords the most convenient method of expressing the *proportionate* strength or precipitating power of each reagent, and one which may be plainly indicated on each bottle.

2. It indicates, as near as can be practically attained, the *actual* strength of each reagent.

Thus:—36 E sulphuric acid contains 36 m.grm. equivalents in 1 c.c., and knowing this we can readily calculate the quantity of any constituent, *e.g.*, the equivalent weight of sulphuric acid being 49, we have $49 \times 36 = 1764$ m.grms. = 1·764 grms. of sulphuric acid present in 1 c.c. Similarly, each c.c. contains $1 \times 36 = 36$ m.grms. = 0·036 grm. of hydrogen, $16 \times 36 = 576$ m.grms. = 0·576 grm. of sulphur, and $32 \times 36 = 1152$ m.grms. = 1·152 grms. of oxygen.

3. By observing the quantity of a reagent employed in an analysis, we can calculate the quantity of by-product therefrom, a point of considerable importance in deciding upon the dilution of our solutions.

For example:—If, during a quantitative analysis, 10 c.c. of 36 E sulphuric acid is added and afterwards neutralised by sodium carbonate, we observe that 10×36 equivalents of sodium sulphate will be produced. Now, since the equivalent of sodium sulphate is 71, we have $71 \times 36 \times 10 = 25,560$ m.grms. = 25·56 grms. as the quantity of anhydrous sodium sulphate formed by the reaction. Knowing this, we are forewarned to dilute sufficiently before proceeding with the analysis.

4. In qualitative analysis we are able to form a better judgment of the amount of substance present than when using the reagents of indefinite strength hitherto employed.

5. The strength of reagents employed in chemical investigations may be most conveniently expressed on this system.

For example:—

Nitric acid sp. gr. 1·4268 at 15·5° C. is *exactly* 16E in strength

"	"	1·1656	"	"	5E
"	"	1·0345	"	"	E

Now it is evident that the latter mode of expression is far simpler, and gives a much more accurate idea of the strength of the acid than does its specific gravity. These equivalent numbers would be a valuable addition to sp. gr. tables.

6. Reagents may be most readily diluted to the various strengths required in chemical analysis.

For example:—Nitric acid sp. gr. 1·42 = 16 E approximately may be readily obtained by distillation. To make an acid of E strength, it is simply necessary to dilute 1 c.c. of 16 E acid with water to the volume of 16 c.c. To make 2 E acid, dilute 2 c.c. of 16 E acid to 16 c.c.; or to make 15 E acid, take 15 c.c. of 16 E acid and dilute to 16 c.c., and so on. This method of dilution, for which I am indebted to Mr. Harris, of Swindon, is applicable to all the reagents, and is theoretically exact. It is not usually necessary to take changes of temperature into consideration, except in the case of strong sulphuric acid.

7. This system affords the simplest method of calculating the theoretical quantity of reagent required to effect any chemical change.

For example:—If we wish to find the quantity of reagent necessary to precipitate 1 grm. of calcium from its solution; we already know that 1 c.c. of E reagent, say E ammonium carbonate, will precipitate 20 m.grms. (1 m.grm. equivalent); consequently, 50 c.c. of E reagent will be required to precipitate 1 grm. If preferred, 10 c.c. of 5 E ammonium carbonate may be used instead. In like manner we can calculate the quantity of acid theoretically required to *dissolve* a given quantity of metal or other substance. Thus, 1 grm. of zinc, containing 30·8 m.grms. equivalents, will theoretically require 30·8 c.c. of E acid or 6·16 c.c. of 5E acid to effect its solution. In the same way it may be shown that while to dissolve or precipitate 1 grm. of thallium theoretically requires only 4·9 c.c. of E reagent, to dissolve or precipitate 1 grm. of beryllium would require 217·4 c.c. of E reagent.

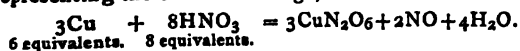
The following table gives the number* of m.grm. equivalents contained in 1 grm. of each of the more common elementary substances. This enables us to find at a glance the number of c.c. of E reagent theoretically required to effect the solution or precipitation of 1 grm. of each substance.

Should a secondary reaction occur, as for instance in the action of copper upon nitric acid, the quantity of re-

* This number is the reciprocal of the equivalent weight $\times 1000$; consequently a table of reciprocals would be applicable for all substances, and might be used for this purpose.

Symbol of Element.	Atomic weight.	Equivalent weight.	M.grm. equivs. per grm., or c.c. of E.
Al'''	27	9	111.1
Sb'''	120	40	25
Sb ^v	"	24	41.7
As'''	75	25	40
As ^v	"	15	66.7
Ba''	137	68.5	14.6
Be''	9.2	4.6	217.4
Bi'''	210	70	14.3
Bi ^v	"	42	23.8
B'''	11	3.67	272.5
Br'	80	80	12.5
Cd''	112	56	17.9
Ca''	40	20	50
C''	12	6	166.7
Ci ^v	"	3	333.3
Cl'	35.5	35.5	28.2
Ce'''	52.5	17.5	57.1
Cr ^{vi}	"	8.75	114.3
Co''	59	29.5	33.9
Co'''	"	19.67	50.8
Cu'	63.5	63.5	15.7
Cu''	"	31.75	31.5
F'	19	19	52.6
Au'	196.6	196.6	5.1
Au'''	"	65.53	15.3
H'	1	1	1000.0
I'	127	127	7.9
Fe''	56	28	35.7
Fe'''	"	18.67	53.6
Pb''	207	103.5	9.7
Li'	7	7	142.9
Mg''	24	12	83.3
Mn''	55	27.5	36.4
Mn ^{iv}	"	13.75	72.7
Mn ^{vi}	"	9.17	109.1
Hg'	200	200	5
Hg''	"	100	10
Ni''	59	29.5	33.9
Ni'''	"	19.67	50.8
P''	31	10.33	96.8
P ^v	"	6.2	161.3
Pt''	197.1	98.55	10.1
Pt ^{iv}	"	49.28	20.3
K'	39.1	39.1	25.6
Si ^{iv}	28	7	142.9
Ag'	108	108	9.3
Na'	23	23	43.5
Se''	87.5	43.75	22.9
S''	32	16	62.5
Si ^v	"	8	125
S ^{vi}	"	5.33	187.6
Sn''	118	59	16.9
Sn ^{iv}	"	29.5	33.9
Tl'	204	204	4.9
Tl'''	"	68	14.7
Ti''	50	25	40
Ti ^{iv}	"	12.5	80
Zn''	65	32.5	30.8

agent required may be deduced from the equation representing the chemical change, as follows:—



Here we see that 6 equivalents of copper require 8 equivalents of nitric acid, or one-third more than the normal quantity; therefore $1\frac{1}{3}$ times the quantity of acid, as obtained from the table, will be required.

8. The system further affords a simple method of calculating the quantity of gas given off in chemical reactions.

Since 1 c.c. of an E reagent, in acting upon excess of metal, will liberate a m.grm. equivalent of hydrogen = 11.16 c.c., the volume given off by x c.c. of any E reagent will

be $x \times 11.16$ c.c. Conversely, we may calculate the quantity of acid required to produce a given volume of hydrogen.

9. In working with this system we have the most convenient method of expressing the precise acidity, &c., of chemical solutions intended for accurate titration, precipitation, &c.

For example:—In Margueritte's method of estimating

iron volumetrically by means of standard $\frac{N}{10}$

potassium permanganate, I recommend that the

solution for titration be acidified to E or $\frac{E}{2}$ sulphuric

acid, thus expressing the acidity at which it is preferred the reaction should take place.

An example of the application of these reagents to the separation of metals may be given. It is known that a solution of zinc chloride containing 1 grm. of zinc in 100 c.c. requires the presence of an appreciable quantity of free hydrochloric acid to prevent the precipitation of the zinc by hydrogen sulphide. It is also known that lead is not completely precipitated from its solutions by hydrogen sulphide if more than 2.5 per cent of free hydrochloric acid be present. The question arises how to acidify the solution so as to allow of the complete precipitation of the lead without the co-precipitation of the zinc. I have found that lead can be completely pre-

cipitated by hydrogen sulphide from an $\frac{E}{2}$ hydrochloric

acid solution without perceptible co-precipitation of zinc,

and now by acidifying the solution to $\frac{E}{2}$ hydrochloric

acid, I always secure the most favourable conditions for the separation of these metals.

As illustrating the application of this system to precipitation, I may mention the determination of lead as sulphate. It is well known that lead sulphate is soluble in strong sulphuric acid, and also in pure water, but that in dilute sulphuric acid it is practically insoluble. The strength of sulphuric acid corresponding to the least solubility does not appear to have been recorded. I have, however, found that lead sulphate is least soluble in E sulphuric acid, and now always adopt this strength in my analytical work.

As a final illustration we will take the precipitation of phosphoric acid by magnesia mixture.

David Lindo, in CHEMICAL NEWS, vol. xlviii., p. 217, has given the conditions under which he considers this precipitation can be best effected. I have calculated the quantities of reagent used in terms of E, and the conditions of precipitation may be stated as follows:—

1st. Solution to be neutral or slightly ammoniacal.

2nd. Dilution of P_2O_5 to be from $\frac{E}{5}$ to $\frac{E}{20}$, or about

1 grm. in from 200 to 800 c.c.

3rd. Dilution of AmCl to be from 0 to $\frac{E}{2}$.

4th. After precipitate has settled, add $\frac{1}{2}$ bulk of $5E$ ammonium hydrate.

5th. Wash with $\frac{3E}{2}$ ammonium hydrate.

6th. Magnesia mixture up to $\frac{E}{3}$ in excess does not

vitiolate result.

7th. Magnesia mixture counteracts solvent action of ammonium chloride.

It is now an easy matter, by means of the equivalent reagents, to ensure that the precipitation shall always take place under the conditions which have been found

to give the best results, and thus secure the highest possible degree of accuracy in our analytical work.

Having now described a system of reagents based on the chemical equivalents, which I have had in use with slight modifications for upwards of twelve years, I beg to recommend them to the attention of analytical chemists. The adoption of some uniform system by which a chemical experiment or method of analysis, once fully described, may be repeated under identical conditions in any laboratory, is a great desideratum. In conclusion, I venture to express the hope that the council of the Chemical Society or the Institute of Chemistry will, ere long, take this subject into consideration, and furnish us with a complete system for general adoption by all workers in chemical science.

Laboratory, L. and N. W. R.,
Crewe, April 4, 1890.

THE COMPOSITION OF BOILER SCALE.*

By THOS. B. STILLMAN.

THE results of an analysis of boiler scale usually represent the lime and magnesia as carbonates with a portion of the former as sulphate—on the general principle that the scale made continues to exist in the form in which it was precipitated. In those portions of the boiler where the direct heat does not come in contact with it, the scale remains unchanged after formation, but the conditions are altered where the scale is subjected to intense heat. In the latter case, while the deposition of the scale-forming material at first occurs as carbonate and sulphate, the gradual heating expels some of the carbonic acid, and the oxides of calcium and magnesium are formed.

That portion of the scale nearest the iron and to the heat loses more of its carbonic acid, and becomes caustic so long as the fire continues.

As soon, however, as the fires are drawn, the oxides of calcium and magnesium become hydrated by absorption of water.

If now a sample of the scale were taken for analysis, the water of hydration becomes an important factor in the analysis:—

A sample of scale from some boilers at Birmingham, Ala., recently submitted to me for analysis gave the following result:—

Silica and clay	11.70 per cent.
Fe ₂ O ₃ , Al ₂ O ₃	2.81 "
CaO	11.62 "
MgO	41.32 "
CO ₂	6.92 "
SO ₃	0.96 "
H ₂ O (of hydration)	21.78 "
H ₂ O (moisture at 212° F.)	0.69 "
Undetermined	0.20 "

Total 100.00 per cent.

An examination of this analysis shows an unusually small amount of carbonic and sulphuric acid, a large amount of water and of magnesia.

The great excess of the latter over the lime indicates that the water from which the scale was formed is a magnesia-water, but its presence in this amount does not in any way alter the conditions of the problem.

With less than 1 per cent of sulphuric acid and less than seven per cent of carbonic acid the oxides of calcium and magnesium could not exist in their entirety as carbonates or sulphates, for, combining the above acids to form carbonates and sulphates, the result indicated over 20 per cent lacking in the 100 parts.

The determinations of the carbonic and sulphuric acids

were in duplicate and in every way satisfactory, while no organic matter of any amount was indicated in the analysis.

The large percentage of the oxides of calcium and magnesium left after combination with the acids suggested water of hydration.

A sample of the scale (dried at 100° C.) was transferred to a platinum crucible and heated over the blast-lamp to a constant weight. The loss of weight was over 28 per cent, and, of course, included the carbonic, but not the sulphuric acid.

To check this result, a sample of the dried scale was ignited in a combustion-tube and the H₂O collected in a weighed chloride of calcium tube. The result was 21.78 per cent. of water of hydration.

This satisfied the conditions existing and the combinations gave as follows:—

Silica and clay	11.70 per cent.
Fe ₂ O ₃ , Al ₂ O ₃	2.81 "
CaSO ₄	1.69 "
CaCO ₃	5.45 "
MgCO ₃	7.36 "
Ca(OH) ₂	13.70 "
Mg(OH) ₂	56.37 "
H ₂ O (moisture at 212° F.)	0.69 "
Undetermined	0.20 "

Total 99.97 per cent.

A section of the scale was subjected to examination, layer by layer, and the following results confirm the above.

That portion of the scale next the iron and nearest the fire contained but traces of CO₂, and was principally the hydrated oxides. The middle portion of the scale was a mixture of CO₂ and the hydrated oxides, while the upper portion of the scale contained carbonates but no hydrated oxides. In other words, the composition of the scale will depend, in a great measure, upon what portion of the boiler the deposit is made. That deposited on the iron or shell not in contact with the flame or not subjected to extreme heat, will remain as deposited—as carbonates and sulphates—while that scale deposited upon the iron, subject to the flame or heat sufficient to drive out any carbonic acid from the scale, will vary in the amounts of CO₂ and water of hydration as indicated.

Scale formed in which the lime all exists as calcium sulphate and in which no magnesium carbonate is present will be subject to but little variation.

TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES.*

By F. A. GOOCH and F. W. MAR.

(Concluded from p. 251).

THE colour of the ferric salt renders it impossible to tell by the appearance of the solution the exact moment when the iodine has been expelled, and starch paper loses its sensitiveness in hot vapours. We bestowed some attention, therefore, upon means for the detection of small amounts of iodine in hot steam in order to avoid the inconvenience of condensing the distillate and testing it for iodine. We found that red litmus, preferably wet, is a most sensitive agent for the detection of iodine under the circumstances, taking on, with exposure to traces of the vapour carrying that element, a distinct grey-blue, deepening with exposure to larger amounts into a

* *Journal of Analytical Chemistry*, Vol. iv., Part 1, January, 1890.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., April, 1890.

Series I.

H ₂ SO ₄ [1:1]. C.m.s.	Fe ₂ (SO ₄) ₃ Grms.	HNO ₃ C.m.s.	KCl = HCl.		KI. Grms.	Initial volume. C.m.s.	Final volume. C.m.s.	Time in minutes.	AgCl found. = HCl found.		Error. Grm.
			Grm.	Grm.					Grm.	Grm.	
10	2*	—	0'4960	0'2425	—	400	300	40	0'9536	0'2425	0'0000
10	2*	—	0'4970	0'2429	—	400	300	40	0'9534	0'2624	0'0005 -
10	2*	—	0'4942	0'2416	—	400	300	30	0'9509	0'2418	0'0002 +
10	2*	2	0'4969	0'2429	—	400	300	30	0'9559	0'2431	0'0002 +
10	2*	3	0'4956	0'2423	I	400	350	30	0'9546	0'2428	0'0005 +
10	2*	3	0'4969	0'2429	I	400	350	23	0'9662	0'2432	0'0003 +
10	2†	3	0'4949	0'2419	I	400	300	27	0'9523	0'2422	0'0003 +
10	2†	5	0'4970	0'2429	I	400	250	55	0'9559	0'2431	0'0002 +
10	2†	5	0'4955	0'2429	I	400	300	30	0'9524	0'2422	0'0000
10	2†	5	0'4967	0'2428	I	400	300	33	0'9546	0'2428	0'0000
10	2†	6	0'4964	0'2427	I	400	300	30	0'9550	0'2429	0'0002

* The iron was added in the form of iron alum.

† The iron was added as FeSO₄ oxidised by HNO₃.

Series J.

H ₂ SO ₄ [1:1]. C.m.s.	NaNO ₂ used in generator. Grms.	KCl = HCl		KI. Grms.	Initial volume. C.m.s.	Final volume. C.m.s.	Time in minutes.	AgCl found. HCl found.		Error. Grm.
		Grm.	Grm.					Grm.	Grm.	
10	2	0'4953	0'2421	I	400	350	20	0'9524	0'2422	0'0001 +
10	2	0'4975	0'2432	I	400	350	16	0'9573	0'2434	0'0002 +
10	2	0'4956	0'2423	I	300	250	15	0'9530	0'2423	0'0000
10	2	0'4973	0'2431	I	300	250	15	0'9550	0'2429	0'0002 -
10	2	0'4964	0'2427	I	300	250	15	0'9550	0'2429	0'0002 +
10	2	0'4969	0'2429	I	300	250	15	0'9567	0'2433	0'0004 +

lavender-blue. The addition of 0'005 grm. of iodine to 400 c.m.³ of boiling water produces immediately upon red litmus-paper the characteristic lavender-blue colour, and the test grows fainter and fainter as fresh test-papers are exposed, until at the end of five minutes, or thereabouts, when the litmus-paper shows no colour, the cooled solution yields no iodine to nitrous acid and chloroform. This reaction of litmus we found of great value, and in no case in which an exposure of two minutes' duration failed to develop the characteristic colour were we able to find iodine in the cooled liquid. To prevent mechanical loss of liquid we made use of the trap described in a previous paper from this laboratory consisting simply of an ordinary two-bulb straight drying tube cut off short and hung with the large end downward in the mouth of the Erlenmeyer flask. The residue in the flask after the expulsion of the iodine was treated with silver nitrate, and the precipitated chloride was determined similarly to that obtained in standardising the solution of potassium chloride.

Several determinations in blank—that is, experiments from which the iodine was purposely omitted—are included, for the sake of comparison, in the tabular statement (Series I).

These eminently satisfactory results prove the trustworthiness of the method.

The fact that nitric acid appears to affect so little the hydrochloric acid in the solution, suggested the possibility that nitrous acid itself might be turned to account and used in a similar process instead of a ferric salt and nitric acid. Some preliminary experiments were made, therefore, to test the behaviour of hydrochloric acid under the action of nitrous acid, and, as they gave favourable indications, the experiments of Series J were undertaken to test the action quantitatively. The general conduct of the test was similar to that followed in Series I. The solution of chloride and iodide containing 10 c.m.³ of sulphuric acid [1:1] was diluted to 400 c.m.³, and agitated while the gas developed by the action of sulphuric acid on 2 grms. of sodium nitrite was passed into it. With pure sodium nitrite at hand, there is probably no serious objection to introducing that substance directly into the solution, but impurities in the article at our disposal made it desirable to generate the gas outside the solution.

For a generator we used two straight drying tubes con-

nected by a rubber tube and set up after the fashion of the von Babo generator, and regulated the rapidity of the current to a rate of five or six bubbles to the second by changing the relative elevation of the generator tubes. The iodine separates immediately upon the introduction of the nitrous fumes and escapes upon boiling in dense fumes, leaving the solution colourless in a very short time. The litmus test was applied as an additional safeguard to indicate the completion of the removal of the iodine. The results of the experiments as given in the accompanying Table (Series J) are evidently satisfactory.

The modes of proceeding to the separation of iodine and the estimation of chlorine according to the processes which we have detailed may be briefly summarised as follows:—

First Method.—To the solution of the alkaline chloride and iodide diluted to about 400 c.m.³ in an Erlenmeyer flask capable of containing a litre, are added 10 c.m.³ of sulphuric acid of half strength, with 2 grms. of ferric sulphate (either in the form of iron alum, or ferrous sulphate oxidised in concentrated solution by about 0'3 c.m.³ of nitric acid), and 3 c.m.³ of nitric acid. A trap, of the form described, is hung in the neck of the flask, and the liquid is boiled until the steam which escapes no longer gives to red litmus-paper, after two minutes' exposure, the characteristic grey-blue due to traces of iodine. Then 1 c.m.³ more of nitric acid is added, and the test for iodine again made. When no iodine is found in the escaping vapour, silver nitrate is added in excess to the contents of the flask, the precipitate is settled, collected in a perforated crucible on asbestos, dried, and weighed as silver chloride.

Second Method.—The solution of the chloride and iodide contained in an Erlenmeyer flask is diluted to 400 c.m.³; 10 c.m.³ of sulphuric acid of half strength are added, and the vapour from 2 grms. of sodium nitrite acted upon by dilute sulphuric acid (preferably in a simple generator, such as is described above) is passed with reasonable rapidity into the agitated solution. The liquid is boiled until colourless, and still further until litmus paper placed in the steam gives no reaction for iodine after an exposure of two minutes. The contents of the flask are treated with silver nitrate, and the precipitated chloride is treated exactly as in the first method.

Both methods are convenient and precise.

SUMMARY OF USEFUL TESTS WITH
THE BLOWPIPE.*By A. J. MOSES.
(Concluded from p. 253).

SULPHUR, S.

On Coal with Soda and a Little Borax.—Thoroughly fuse in the R. F., and either—

- (a) Place on bright silver, moisten, crush, and let stand. The silver will become brown to black. Or
- (b) Heat with dilute HCl (sometimes with powdered zinc); the odour of H_2S will be observed.

In Open Tube.—Suffocating fumes. Some sulphates are unaffected.

In Closed Tube.—May have sublimate red when hot, yellow cold, or sublimate of undecomposed sulphide, or the substance may be unaffected.

With Soda and Silica (equal parts). A yellow or red bead.

To Determine whether Sulphide or Sulphate.—Fuse with soda on platinum foil. The sulphide only will stain silver.

TELLURIUM, Te.

On Coal.—Volatile white coat with red or yellow border. If the fumes are caught on porcelain, the resulting grey or brown film may be turned crimson when moistened with conc. H_2SO_4 and gently heated.

On Coal with Soda.—Thoroughly fuse in R. F. Place on bright silver, moisten, crush, and let stand. The silver will be blackened.

Flame.—Green.

In Open Tube.—Grey sublimate fusible to clear drops.

With H_2SO_4 (conc.).—Boiled a moment, there results a purple violet solution, which loses its colour on further heating or on dilution.

TIN, Sn.

On Coal.—O. F., the oxide becomes yellow and luminous.

R. F., a slight coat, assisted by addition of sulphur or soda.

With Cobalt Solution.—Moisten the coal in front of the assay with the solution, and blow a strong R. F. upon the assay. The coat will be bluish green when cold.

With CuO in Borax Bead.—A faint blue bead is made reddish brown or ruby-red by heating a moment in R. F. with a tin compound.

Interfering Elements.

Lead or Bismuth (Alloys).—It is fair proof of tin if such an alloy oxidises rapidly with sprouting and cannot be kept fused.

Zinc.—On coal with soda, borax, and charcoal in R. F. the tin may be reduced, the zinc volatilised; the tin may then be washed from the fused mass.

TITANIUM, Ti.

With Borax.—O. F., colourless to yellow hot, colourless cold, opalescent or opaque-white by flaming.

R. F., yellow to brown, enamel blue by flaming.

With S. Ph.—O. F., as with borax.

R. F., yellow hot, violet cold.

HCl Solutions.—If insoluble the substance may first be fused with S. Ph. or with soda and reduced. If then dissolved in dilute acid and heated with metallic tin, the solution will become violet after standing. Usually there will also be a turbid violet precipitate, which becomes white.

Interfering Elements.

Iron.—The S. Ph. bead in R. F. is yellow hot, brownish red cold.

TUNGSTEN, W.

With Borax.—O. F., colourless to yellow hot, colourless cold, can be flamed opaque-white.

R. F., colourless to yellow hot, yellowish brown cold.

With S. Ph.—O. F., clear and colourless.

R. F., greenish hot, blue cold. On long blowing or with tin on coal, becomes dark green.

With Dilute HCl.—If insoluble the substance may first be fused with S. Ph. The solution heated with tin becomes dark blue; with zinc it becomes purple and then reddish brown.

Interfering Elements.

Iron.—The S. Ph. in R. F. is yellow hot, blood-red cold.

URANIUM, U.

With Borax.—O. F., yellow hot, colourless cold, can be flamed enamel yellow.

R. F., bottle-green, can be flamed black, but not enamelled.

With S. Ph.—O. F., yellow hot, yellowish green cold.

R. F., emerald green.

Interfering Elements.

Iron.—With S. Ph. in R. F. is green hot, red cold.

VANADIUM, V.

With Borax.—O. F., colourless or yellow hot, greenish yellow cold.

R. F., brownish hot, emerald-green cold.

With S. Ph.—O. F., dark yellow hot, light yellow cold.

R. F., brown hot, emerald-green cold.

H_2SO_4 Solutions.—Reduced by Zn become successively yellow, green, bluish green, blue, greenish-blue, bluish violet, and lavender.

ZINC, Zn.

On Coal.—O. F., the oxide becomes yellow and luminous.

R. F., yellow coat, white when cold, assisted by soda and a little borax.

With Cobalt Solution.—Moisten the coal in front of the assay with the solution, and blow a strong R. F. upon the assay. The coat will be bright yellow-green when cold.

Interfering Elements.

Antimony.—Remove by strong O. F. or by heating with sulphur in closed tube.

Cadmium Lead or Bismuth.—The combined coats will not prevent the cobalt solution test.

Tin.—The coats heated in an open tube with charcoal dust by the O. F. may yield white sublimate of zinc.

ON SOME APPLICATIONS OF CAUSTIC
SODA OR POTASH AND CARBON IN THE
QUALITATIVE AND QUANTITATIVE
ANALYSIS OF MINERALS.*

By CHARLES A. BURGHARDT, Ph.D.

To those chemists who are brought much into contact with minerals and metallic ores, it has been for a long time a desire that the processes by which such minerals are made available for analysis should be rendered short, accurate, and simple. The minerals I refer to, of course, are those which are insoluble in acids. As is only too well known to chemists, a considerable expenditure of time and much patience is often required before the desired splitting up of the mineral and its solution is arrived at. There are, generally speaking, three kinds of fusing-mixtures or fluxes which the chemist has at his

* From the *School of Mines Quarterly*, vol. xi., No. 1.* From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, Vol. iii., Fourth Series, Session 1889-90.

disposal (for it is necessary to fuse the refractory mineral at a high temperature for a long time with one or more of these fusing mixtures), the commonest fusing mixture being one consisting of carbonate of sodium and nitrate of potassium, and most minerals can be eventually split up by its action. Some minerals are only acted upon by being fused with hydrogen potassium sulphate, it sometimes being necessary to split up partially with the first-mentioned fusing mixture, the process being finished by fusing the insoluble still refractory residuum with the hydrogen potassium sulphate. With many minerals these reactions are not complete even after several fusions at a long-sustained very high temperature. This entails much labour at the blowpipe table, and annoyance if the results obtained are not satisfactory. I am aware that many methods have been devised for arriving at satisfactory results by modifying, in various ways, the well-known fusion processes, but so far without very much real improvement.

I venture now to lay before you a general process which deals with all the refractory silicates, several refractory oxides and compounds of oxides, and some other insoluble mineral compounds. I am still occupied in ascertaining whether this process is applicable in the case of minerals where sulphur, arsenic, and antimony enter largely into their composition, and hope later on to lay the results obtained before this Society. After many experiments, I found that the best results were obtained by mixing the finely-divided mineral with about 10 per cent of its weight of finely-divided charcoal, and projecting the mixture carefully into a silver crucible containing fused hot caustic soda or potash, about six times the weight of the mineral powder taken for analysis. The crucible and its contents are then carefully heated over an ordinary Bunsen burner until the reaction arising has taken place, this point being easily ascertained by the fact that all further evolution of combustible gas has ceased, and the mass remaining in the crucible has become dry, and generally white or grey in colour. From the experiments which I have made I conclude that hydrogen gas is evolved from the caustic alkali, and possibly a small quantity of carbon monoxide, whilst undoubtedly carbon dioxide is largely produced by the combination of the carbon with the oxygen of the caustic alkali and the oxygen of the oxides present in the minerals taken for analysis. Further there is no doubt in my mind that metallic sodium or potassium is liberated during the course of the reaction, and these metals, whilst in the *status nascendi*, combine either with the metallic oxide (as in the case of oxide of zinc and oxide of tin) or with the acid present in the minerals. The latter conclusion will be more apparent after describing in greater detail the various experiments which I have made.

Quantitative Analysis of Tin Ore from Cornwall.

Two samples of roasted so-called black tin were powdered to an exceedingly fine powder and submitted to the process sketched out above. Black-tin is the technical term applied to tin ore which has been concentrated by washing away the lighter mineral impurities, drying, and afterwards roasting to free it from sulphur, arsenic, and antimony.

I took 0.5 grm. of the sample, mixed it carefully with sufficient powdered charcoal, and added the mixture carefully to the melted hot caustic alkali (soda was used in most cases) in the silver crucible. Heat was then gently applied with an ordinary Bunsen burner, and the mass heated until no further evolution of burning gas was observed; generally, thirty minutes heating being sufficient. The crucible and its contents were then placed in a porcelain basin, and the contents dissolved out with distilled water, and filtered from the insoluble oxides, undecomposed carbon, &c. I always submitted the residue to a second fusion, and found in most cases that every trace of mineral was completely decomposed after the

second fusion. In the solution were silicate of sodium, aluminate of sodium, and stannate of sodium, whilst in the insoluble residue were silica, bismuthic oxide, cupric oxide, ferric oxide, calcium carbonate, and manganese dioxide. The details of the method of analysis of the insoluble residue it will be unnecessary for me to enter into here, whilst the analysis of the soluble portion simply resolved itself into the elimination of the silica from the solution (previously treated with hydrochloric acid in excess) in the usual manner, the precipitation of the tin as sulphide, and its subsequent conversion into stannic oxide, in which form it was weighed.

The analyses resulted as follows, viz. :—

Sample.	No. 1.	No. 2.
Stannic oxide (SnO ₂)	66.04	82.84
Silica	14.80	4.20
Manganese dioxide	1.90	none
Ferric oxide	13.60	8.04
Cupric oxide	2.48	4.20
Calcium oxide	0.40	none
Bismuthic oxide	0.08	1.28
	99.30	100.56

I found that 95 per cent of the total tin in the ore was taken up in the first fusion, which I consider a very satisfactory yield. By the old method of analysis the fusion would have to be performed over a blowpipe for an hour or more, and repeated at least three times in order to extract all the tin. *For success either by the old process or by my process an extremely fine state of division of the sample is necessary.*

Quantitative Analysis of Wolframite.

This mineral is practically tungstate of iron. It is a difficult mineral to analyse by the old methods, and much time is required to carry out the different processes. By my process the iron is entirely separated from the tungstic acid at once, and remains behind (after solution of the melt and subsequent filtration) on the filter-paper as ferric oxide and magnetic oxide. The greater portion of the manganese present in the mineral is also found on the filter-paper as manganese dioxide with the iron. In the solution there is tungstate of sodium, manganate of sodium, and silicate of sodium. The tungstic acid is thrown out of this solution (along with any niobic acid which may be present) by adding a slight excess of hydrochloric acid and boiling, when the tungstic acid, WO₃, is precipitated out as a yellow powder, dried, ignited, and weighed. Of course, if niobic acid is present, it must be separated from the tungstic acid.

A specimen of wolframite on analysis by the new method furnished the following result, viz. :—

WO ₃	64.00
FeO	17.51
MnO	11.67
SiO ₂	7.20
	100.38

In this analysis I think the error is due to the silica being too high.

Quantitative Analysis of Chrome Iron Ore.

I have not had time to completely analyse the sample operated upon by the new process, but append the results, as below, the silica and alumina being obtained by difference. I varied the general method in this special instance by adding ammonium nitrate to the solid caustic soda before introducing the same into the silver crucible. This addition of the ammonium nitrate is to cause the chromic oxide liberated to be at once oxidised to chromic acid and combined with the excess of caustic soda present, thus forming sodium chromate. The method of working is briefly as follows :—

The finely divided levigated sample was mixed with

10 per cent of its weight (0.5 grm. of chrome iron ore was taken) of powdered charcoal and placed into the silver crucible, then five or six times the weight of caustic soda and about three times the weight of the substance taken of ammonium nitrate were placed upon the mineral in the crucible, and the whole heated gently at first, afterwards to redness for half-an-hour or so over the ordinary Bunsen burner. The cooled mass was afterwards extracted with water, filtered, and the solution evaporated down to dryness in a platinum basin, with ammonium nitrate to separate the alumina and silica, which were then filtered off. The filtrate from this treatment was rendered acid with hydrochloric acid, when *chromic chloride* was at once obtained without reduction by means of a reducing medium, and the chromium was precipitated out by means of ammonia, filtered off, the precipitate dried, ignited, and weighed as Cr_2O_3 . I cannot at present explain this remarkable reduction of the chromic acid, because in some experiments I had to employ a reducing medium as usual, such as boiling the acid solution with a little alcohol. I hope to investigate this reaction further. The results obtained are as follow, viz. :—

Cr_2O_3	43.40
FeO	19.44
MgO	8.86
Alumina and silica .. .	28.30
	100.00

After the fusion and extraction with water, the insoluble matter on the filter-paper was ferric oxide, magnesium carbonate, carbon, &c.

Qualitative Experiments.

Rutile (TiO_2) was at once decomposed and titanite of sodium produced, which, on being acidified with hydrochloric acid, gave the various reactions for titanium; for instance, a portion of the solution, on having a piece of metallic tin placed in it, gave a fine purplish-red coloured solution.

Titanite of Iron or Ilmenite gave the same reactions for titanium. It was easily attacked by the method.

Barytes (BaSO_4) gave insoluble carbonate of barium, which was then filtered off and dissolved in hydrochloric acid and tested with sulphuric acid, when it at once furnished a precipitate of barium sulphate. The filtrate from the barium carbonate, on being tested with hydrochloric acid, did not give off any sulphuretted hydrogen, proving the *absence* of sodium sulphide; therefore no reduction of the sulphuric acid had taken place. On testing the acidified solution, sulphuric acid was detected in large amount, consequently sodium sulphate had been found.

Simple silicates, such as kaolin (china-clay), talc, cyanite, &c., and double silicates such as tourmaline, hornblende, garnet, &c., are split up and rendered soluble just as easily as any of the other minerals mentioned above. I hope at some future time to lay before the Society a more extended series of analyses of metallic ores and silicates, also of some minerals containing fluorine, by the new method, and in concluding this communication I must express my thanks to my young assistant, Mr. Gilbert Rigg, who has carried out my instructions with great intelligence and enthusiasm.

A New Method of Chlorinisation in the Aromatic Series.—M. Petricou.—The author chlorinises benzene by means of tin chloride in the nascent state. He introduces into a flask terminating in an ascending condenser 400 c.c. of pure benzene and 90 grms. of granulated tin. He then introduces a current of tin and slightly heats the mass. After forty-nine hours of reaction the tin had disappeared and the benzene was become a mass almost solid at the common temperature.—*Bull. de la Soc. Chim. de Paris*, Vol. iii., No. 4.

PROCEEDINGS OF SOCIETIES

PHYSICAL SOCIETY.

May 16, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

PROFESSOR W. COLEMAN was elected a member of the Society.

Lord RAYLEIGH exhibited and described an arrangement of "Huyghen's Gearing in Illustration of Electric Induction."

This gearing consists of two loose pulleys mounted on the same axle, with an endless cord laid over them, the loops or bights of which carry weighted pulleys whose planes are parallel to the axis on which the upper pulleys turn. If one of the latter pulleys be started to rotate, the other one turns in the opposite direction until such time as the speed of rotation of the first one becomes constant. Whilst this constant speed is maintained the second pulley remains stationary, one weight being raised and the other lowered; but, on retarding the motion of the first pulley, the second begins to turn in the same direction as the first. It will be noticed that the phenomena are analogous to those which occur in electric induction, where starting or increasing a current in one circuit induces an opposite current in a neighbouring circuit, whilst decreasing or stopping a current induces one in its own direction. Lord Rayleigh pointed out that in this apparatus there is nothing strictly analogous to electric resistance, for the friction does not follow the same law. The analogy, he said, was complete as regards there being no change of potential energy, and the mathematical equations for the kinetic energy of the system are precisely the same as those given by Maxwell for electric induction.

Dr. S. P. THOMPSON made a communication on "Dr. Kœnig's Researches on the Physical Basis of Music," in the course of which Dr. Kœnig performed numerous novel and interesting experiments clearly illustrating the subject to a crowded audience.

After referring to the classical researches of the great mechanician, and to the remarkable precision with which his ingenious and unique acoustical apparatus is constructed, Dr. Thompson said the subject with which he wished to deal could be divided into two parts, the first relating to *Beats* and the second to the *Timbre* of sounds. On the question of beats, considerable discussion had taken place as to whether they formed independent tones if they were sufficiently rapid. Different authorities had come to different conclusions on the subject, the disagreement probably arising from the impure tones used in these investigations. Dr. Kœnig, however, had succeeded in making tuning-forks whose sounds are very nearly pure tones, and, by the aid of such forks, had conclusively answered the question in the affirmative. Before proceeding to show experimentally the truth of the conclusions arrived at, Dr. Thompson said it was necessary to define exactly the meaning of the term "harmonica." By this he meant tones whose frequencies are *true integral multiples* of their fundamental. This, he said, might seem to be identical with the "upper partial tones" of Helmholtz or the "overtones" of Tyndall; but such was not the case, as the upper partial tones of piano wires, &c., are not true integral multiples of the fundamentals, for the rigidity of the wire comes into play and prevents the sub-division being exact.

According to Helmholtz's theory, two tones harmonise when they do not produce beats of sufficient slowness to grate upon the ear, and the frequency of the two sets of beats were supposed to be equal to the difference and the sum of the frequencies of the two fundamental tones. In investigating the subject, Kœnig finds it necessary to distinguish between primary and secondary beats, and also

that primary beats belong to two categories. These categories he calls inferior and superior respectively, and the frequencies of the two sets correspond respectively to the positive and negative remainders obtained by dividing the number representing the number of vibrations in the tone of lowest pitch into the corresponding number for the higher tone. For example, two forks of 100 and 492 vibrations produce beats having 92 and 8 as their vibration frequencies for—

$$492 = 100 \times 4 + 92$$

$$\text{and also } 492 = 100 \times 5 - 8$$

A set of "superior" beats of 8 per second and an inferior beat tone of 92 per second may be heard when two such forks are sounded together. These primary beats or beat tones act as independent tones, and produce secondary beats. Tertiary ones may also be obtained.

To demonstrate the existence of beats to the large audiences assembled, Dr. Koenig had provided two large tuning-forks with resonators about four feet long. One of the forks gave 64 vibrations per second and the other 128, but the latter had sliding weights whereby its frequency could be made anything between 128 and 64. Adjusting the weights so as to give 72, and bowing both forks, the beats of about 8 per second were distinctly heard at the extremity of the room. By varying the weights so that the fork gave 80, 85½, 96, 106½, 112, 120, and 128 vibrations successively, beats of various frequencies were produced, and it was remarkable to note that tones of 64 and 120 produced 8 beats a second, exactly like 64 and 72. When the forks made 64 and 96 vibrations, i.e., at an interval of a fifth, then the inferior and superior beats agree in frequency, viz., 32, and by careful observation a low tone of about this pitch can be heard. If the tones sounded simultaneously differ by more than an octave, the same law for the number of beats holds good, whilst Helmholtz's difference and summation tone law is inapplicable. This was shown by sounding a fork and its double octave slightly mistuned by weighting; slow beats were quite evident, although the difference in the frequencies of the primary notes was large. Similarly, forks vibrating approximately at rates in the proportions 1 : 5 and 1 : 6 gave slow beats.

Coming to the main question, as to whether beats, when sufficiently rapid, blend into tones, just as primary shocks do, Dr. Thompson briefly recalled the various arguments for and against such an effect; and then Dr. Koenig proceeded to experimentally prove the affirmative. Taking two forks, tuned to 2048 and 2304 vibrations respectively (ratio 8 : 9), and sounding them simultaneously, the middle C of the piano (256) was distinctly heard. The same beat tone resulted from forks having frequencies in the ratio of 8 : 15, whose negative remainder was 256. Various other tones were sounded simultaneously in pairs, and in all cases the corresponding beat tone was quite distinct. In these experiments the existence of nodes and loops in the air was distinctly noticeable, for as Dr. Koenig turned the tuning forks in his hand the intensity of the beat tones heard at a particular spot varied enormously. The experiments were carried a step further by impressing vibrations of different frequencies on one and the same body; the beat tones in this case were quite perceptible. In carrying this out Dr. Koenig had constructed steel bars of approximately rectangular section, whose periods of vibration were different in two directions at right angles: striking one face of the bar a certain note resulted, whilst a blow on an adjacent face produced a different one. When the bar was struck on the edge adjoining the two faces both of the notes could be heard as well as the beat tone produced therefrom. The experimenter had gone still further and made such bars so short that neither of the fundamental notes are within the limits of audition, but the resulting beat tones can be heard quite distinctly. In all cases, the frequency of the beats agree with that calculated from Dr. Koenig's formula, and secondary beats follow the same law.

It was then pointed out that not only beats, but the maxima of a series of pulsations varying in intensity will, if isochronous and sufficiently rapid, give tones just as a series of primary shocks do. This was illustrated by tuning forks and by directing a stream of air issuing from a slit against a notched rim of a rotating disc. A further modification was given by a modified disc siren; in this the holes, instead of being of the same size all round a circle, increase to a maximum and then decrease again, there being several sets of such holes in one circumference. When this was put in operation, notes corresponding in pitch to the number of holes, and also to the number of sets of holes, could be heard. A wave siren was also used to illustrate the same facts. The matter was further illustrated by moving a tuning fork towards a wall or other reflecting surface at various velocities. According to Doppler's principle, as the fork recedes from the observer and approaches the wall the frequency of the direct waves is less and that of the reflected waves greater than that of the fork, and these two series of waves produce beats. By sufficiently increasing the velocity and using a fork of high pitch, the beats blend into tones.

Coming to the second half of Dr. Koenig's researches, Dr. Thompson said that Helmholtz contended that the "timbre" of musical sounds was not affected by differences of phase amongst the component tones; on this point, however, Koenig had come to the opposite conclusion. To illustrate graphically why phase should affect timbre, a number of diagrams were exhibited, some showing the resultant wave form produced by combining a tone with its harmonics of equal intensity, when the differences of phase between them were 0, ½, 1, and 2 respectively, while others represented the wave-forms when the harmonics and the fundamental were of different intensities. The effect of phase on the shape of the wave-form was very marked. The subject was treated experimentally by means of a wave-form against which a stream of air issuing from a slit could be directed. By inclining the slit to one side of the radius or the other, the phases of the component waves could be altered, and this had a marked effect on the character of the sound produced. Illustrations of Koenig's multiple wave-sirens, both of the cylinder and disc forms, were next shown, and the results of investigations made with the apparatus described. From these results it appears to be impossible to produce the timbre of instruments such as trumpets, clarionets, &c., by any combination of a tone and its pure harmonics. This led to the investigation of impure harmonics. By plotting and combining curves it was shown that the wave-form obtained from a tone and impure harmonics changes in successive periods, and this peculiarity was observed to exist in a record taken from a vibrating string. Various discs with wavy edges of different forms were spun before an air slit, and the varying character of the resulting sounds as the slit was turned, demonstrated.

Before concluding, Dr. Thompson remarked the word "timbre" required to be re-defined, for the rigidity of strings, wires, &c., and the interference of the wood and metal parts of organ pipes and other wind instruments generally, prevent the formation of pure harmonics. A model, consisting of vibrating strips placed vertically or inclined, was exhibited to show the different kinds of timbre. The difference between mixtures and compounds of tones was pointed out, and the inability of the ear to distinguish between pure and impure sounds referred to.

Lord RAYLEIGH thought more information was required on the important subjects brought forward, and asked in what class of musical sounds are the overtones strictly harmonious. He could admit that in piano wires they may not be so, but he was not quite so clear about organ pipes. He said he was filled with admiration with the perfection of the apparatus displayed, and expressed a wish that such mechanical acousticians could be found on this side of the channel.

Mr. BOSANQUET said he had been carefully over the

ground investigated by Dr. Koenig. He believed Dr. Koenig was the first to get at the facts concerning beats, but it was difficult to admit all that had been said about them. However, the chief difference between authorities seemed to be one of language. Owing to the lateness of the hour he could not discuss the question fully, and so asked to be allowed to reserve his opinion on the matter. As regards "timbre" he thought the experiments on the effects of phase were not conclusive. The sounds of wind instruments, such as trumpets, he said, depended greatly on who produced them. It was no easy matter to bring out their full sweetness, and it was comparatively few persons who could ever attain perfection. He ventured to think that in a properly used instrument none of the harmonics are out of tune.

Mr. BLAKLEY agreed with Lord Rayleigh about piano wires, and, as regards wind instruments, he would hardly think that the overtones were so inharmonious as Dr. Thompson would have him believe. In fact, Mr. Stroh had obtained wave-forms for him from various instruments, but in none of them was there any discontinuity such as shown on one of the diagrams exhibited. However, he was of opinion that there is something in "timbre" not accounted for by the ordinary theory.

The PRESIDENT said that in view of the production of audible sounds by the beats from notes beyond the range of audition, it might be possible to demonstrate that insects produce sounds inaudible to the human ear by putting several together in a box and listening for beat tones.

Dr. KÖNIG acknowledged the most cordial vote of thanks accorded to himself and Dr. Thompson.

CORRESPONDENCE.

TAR ACID IN VINEGAR.

To the Editor of the Chemical News.

SIR,—A few days back a sample of malt vinegar was submitted to me for examination. Analysis gave the following results per cent:—

Solid matter	1.20
Acetic acid	4.46
Ash	0.14
Sp. gr.	1.0119

No free sulphuric acid—no injurious metals. These results are in fair accordance with those of a genuine malt vinegar, and I felt justified in regarding it as such.

Out of curiosity, and luckily, I tasted the vinegar, and noticed after a time, when the pungent taste of the acetic acid had disappeared, a lingering flavour strongly resembling tar acid. On distilling I then obtained a distillate which readily yielded tribromocresol with bromine-water. The iron reaction was not distinct, nor could the smell of tar acid be detected, probably on account of the presence of acetic acid. I do not remember reading anywhere of vinegar containing such a foreign substance as cresolic acid, and it is just a question whether, in the present case, its existence was accidental or purposed. The probability of it being overlooked, when present in small quantity, in carrying out the ordinary analysis of vinegar, renders it, I venture to think, worthy of the notice of your numerous readers.—I am, &c.,

S. ARCHD. VASEY.

Chandos Street, London, W.C.,
May 20, 1890.

Action of Sulphuric Acid upon Tribromo-phenol.—M. Georgesco.—The author finds, in opposition to Hertzog, that sulphuric acid does not destroy tribromo-phenol, but transforms all the bromo-derivative into francine.—*Bull. de la Soc. Chim. de Paris*, Vol. iii., No. 4.

NOTICES OF BOOKS.

The Chemistry of Paints and Painting. By A. H. CHURCH, M.A., F.R.S., Professor of Chemistry in the Royal Academy of Arts in London. London: Seeley and Co., Limited.

We have much pleasure in welcoming a work on this subject from the pen of a distinguished chemist, who has made it his special study.

Our first emotion on examining Prof. Church's treatise was surprise at finding some of the colours recognised by the dyer and tissue-printer as "fast," such as indigo and madder, here regarded as untrustworthy. But it must be admitted that the conditions in the two cases are totally different. A tinctorial masterpiece is exposed to the light, perhaps for a few days or weeks. At the end of that time the pattern or the shade or the garment goes "out of fashion," and whether the colour has proved permanent or not no one cares to inquire. The works of the artist are much more severely tested. They are exposed to light continuously, perhaps, for half a century, and if their colours are not absolutely permanent they cease to be "things of beauty," and become rather an eye-sore than "a joy for ever."

The author, in his strictness, is guided not merely by theoretical considerations or even by prolonged experiments, but by the careful study of the changes which have taken place in pictures by the most eminent masters. Hence the advice which he gives should be taken to heart by every artist who aims at something more than transitory effects. Thus he says:—"Beautiful and rich as are the colours prepared from cochineal, not one of them should ever find place upon the palette of the artist. They all become brownish, and ultimately almost disappear after a short exposure to sunlight. Ultimately, a greenish grey or a faint sepia-like brown is the sole residue." The madder-colours are said to be "much less affected by light than are the pigments from cochineal, yet it cannot be affirmed that any of them are absolutely permanent when continuously exposed."

Indigo is "unfortunately gradually oxidised and browned when exposed to light." Hence Prof. Church does not recommend it, and suggests that it may be advantageously replaced by ultramarine or by a good prussian blue, either being associated with a little ivory black.

Guignet's green, otherwise known as vividian, is pronounced to be in every respect a safe pigment. Unfortunately, it is sold in France under the name of "*vert émeraude*," one of the synonyms of Schweinfurt green, and, what is still worse, vile mixtures of chrome yellow and prussian blue are sometimes sold in its place.

Among yellows, cadmium sulphide, when genuine and properly prepared, seems to take the first rank. Vanadium yellow, though in every other respect admirable, loses its beauty if exposed to light for a few hours only.

Among whites must be noticed a curious novelty—lead sulphate prepared by a special process. It is said to be less readily acted upon by sulphuretted hydrogen than is ordinary white lead. Zinc white (sulphide) is objected to from its injurious action upon many other colours.

It is quite natural that the vermilions heightened by an admixture of eosine, geranium red (mercuric iodide), and the aniline lakes should be excluded. But we regret that there is no mention of "mineral lake," a stannic chromate, described by Gentele as very similar in its colour to rose madder, whilst perfectly fast.

It is interesting to find that certain choice madder-pigments for artists have still to be prepared from the plant in preference to artificial alizarin. Were this not the case the cultivation of *Rubia tinctorum* would be "wholly extinguished."

Among the most important features of this work is a selection—or rather several selections—of pigments

which may be regarded as, under ordinary circumstances, fully permanent. The work concludes with a notice of a long and somewhat acrimonious discussion on the stability of water-colour drawings, which raged in 1886 in the *Times* and in several other papers.

Artists and lovers of art will the better appreciate Prof. Church's book if they reflect that its chief rival is a treatise in which vermilion is described as a "sulphide of arsenic," and in which, when testing for lead in cadmium red, the operator is advised first to add white lead to the sample. It is to be regretted that the modern rage for apparent cheapness will oppose a barrier to the selection of suitable pigments and the elimination of such as are untrustworthy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 19, May 12, 1890.

Iridium and Phosphorus Double Chloride.—H. Geissenheimer.—The author uses as his material the hydrated dioxide. He heats 1 grm. of this hydrate for thirty hours in a sealed tube with 10 grms. phosphorus perchloride and 15 grms. of phosphorus trichloride. He obtains light yellow crystals of the formula $\text{Ir}_2\text{P}_2\text{Cl}_{15}$, which, if kept for half an hour between 70° and 80° , are converted into $\text{Ir}_2\text{Cl}_3 \cdot 2\text{PCl}_5$. At temperatures between 120 and 125 the product is $\text{Ir}_2\text{Cl}_3\text{PCl}_5$. If the temperature is gradually raised to 190° , the chloride becomes brick-red, and corresponds to the formula $\text{Ir}_3\text{Cl}_3\text{PCl}_5$.

A New Characteristic Reaction of Hydrogen Peroxide.—G. Denigès.—An aqueous solution of ammonium molybdate (10 per cent) to which an equal volume of concentrated sulphuric acid is added gives, on the addition of a few drops of oxygenated water, an intense yellow colouration resembling that of the alkaline dichromates. It enables us to detect 1-10th m.grm. of hydrogen peroxide.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 4.

Researches on the Sulphines.—G. Patein.—The author has obtained four double cyanides of sulphines and silver, which he here describes.

New Chemical Properties of the Alcoholic Extract of Beer Yeast.—J. de Rey-Pailhade.—The author, on stirring up beer-yeast, previously washed and pressed, in an equal weight of alcohol at 86° , and filtering, obtains a liquid of a light yellow colour, clear, and having a slightly acid reaction. This liquid he names *philothion*. If shaken up with washed sulphur or with ether saturated with sulphur it gives off sulphuretted hydrogen. One litre of the liquid recently prepared yields about 10 m.grms. of H_2S . The alcoholic extract of yeast, if exposed to the air for a few days, loses this property of combining with or taking up sulphur.

Speed of Dissolution of Certain Mineral Carbonates in Acids.—W. Spring.—All the carbonates tried (arragonite, witherite, cerusite, azurite, dolomite, smithsonite, and malachite) dissolve with equal speed in hydrochloric and nitric acids. The rate of solution is independent of the chemical nature of the inorganic monobasic acids, or the rate of solution is a constant magnitude for each species of carbonate. The phenomenon depends on physical and not chemical factors. The rate of solution increases rapidly with the temperature, but in an un-

equal manner in different carbonates. Hence a comparison of the rates of solution of the carbonates at given temperatures cannot yield any result of a general scientific value.

Rate of the Solution of Iceland Spar in Hydrochloric Acid.—W. Spring.—The rate of the solution of spar in an acid does not merely depend on the chemical nature of the mineral, but is also a simple function of the elasticity, and varies with the temperature according to an exponential.

Action of Fuming Nitric Acid upon Hexachloric Benzene.—M. Istrati.—The author has succeeded in causing nitric acid to act upon hexachlorobenzene. He concludes that chlorine, though intimately connected to the molecule, may be partially expelled by nitric acid and replaced by oxygen. During the attack there is produced a gaseous mixture of nitrous vapours, and probably carbon dioxide, free oxygen, and nitrogen.

Transformation of Paradichlorobenzene into its Meta-Isomer.—M. Istrati.—Not suitable for useful abstraction.

New Method for the Preparation of Non-saturated Acids of the Aromatic Series.—L. Eddeleano and M. Budishteano.—The authors have sought to combine the methods of Bertagnini and of Perkin. They heated benzoic aldehyd with acetyl chloride in the proportion of 1 mol. with 3 mols. sodium acetate, heating for twenty-four hours to 160° in a flask with an ascending condenser.

Melting and Solidification-Points of Certain Fatty Bodies and of their Mixtures.—A. Terreil.—The author's results are given in the form of tables.

The Refractive Molecular Powers of Salts in Solution.—E. Doumer.—Already noticed.

On Azocumyl Chloride.—P. Alexeyeff.—The chlorides of the azo-acids give us not merely a means of preparing their derivatives, but also of purifying the azo-acids and of establishing their molecular weights.

Vol. iii., No. 5.

Physiological Action of Selenious Acid.—C. Chabrie and L. Lapique.—A dose of selenious acid a little above two-thousandths is needed to hinder the fermentation of meat-broth under the action of the ordinary microbes of the air. With smaller proportions fermentation is set up and the selenious acid is reduced. Sulphites injected into the blood of an animal are converted into sulphates, which has no poisonous action. The selenites are not oxidised under similar conditions. In the higher animals selenious acid has a very considerable poisonous action. Dogs die when they have received 3 m.grms. of neutral sodium selenite per kilo. of their weight. There is intense congestion of all the viscera. The heart is arrested in systole.

Natural Manganese Oxides. Psilomelanes and Wads.—A. Gorgeu.—Among the minerals known as "wads," some affect a crystalline form, and there is no warrant for considering them, as alteration-products. They are true acid hydrated manganites answering to the formulæ:—



Researches on Dispersion in the Aromatic Compounds.—Ph. Barbier and L. Roux.—This paper requires the accompanying diagram and tables.

Vol. iii., No. 6.

Determination of Total Nitrogen in Manures.—E. Aubin and J. Quenot.—This paper will be inserted in full.

The Synthesis of Ethyl α - β -Diacetylpropionate.—Iw. Ossipoff.—The author has obtained this product by setting out from sodium ethyl acetyl acetate, which is treated with monochloro acetone.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. viii., No. 2.

Recent Progress of the Electro-Metallurgy of Aluminium and the Influence of this Metal upon Siderurgic Products.—R. van Langhenhove.—The author calls attention to the extraordinary fact that when aluminium is once deoxidised it becomes difficultly oxidisable, even at the highest temperatures. He concludes that in forming ferro-aluminium alloys only small proportions of the latter metal should be introduced. Aluminium acts upon iron in the same manner as carbon, increasing its hardness and tenacity at the expense of ductility. In augmenting fluidity and ensuring the absence of blowholes its action is similar to that of silicon. Phosphorus, like silicon and copper, occasions more or less serious perturbations in castings containing aluminium.

Vol. viii., No. 3.

Resistance of Aluminium-Bronze and Brass.—M. Tetmayer.—As the proportion of aluminium rises from 5.5 to 11.5 per cent in bronzes, the resistance to rupture per m.m. rises from 44 to 80 kilos. In the case of brass, as the percentage of aluminium increases from 1 to 4 per cent the resistance rises from 40 to 69 kilos. per m.m.

Vol. ix., No. 1.

Chemical Industry at the Paris Exhibition of 1889.—Jean Kruitweg.—The author expresses his regret at the "indifference" of Switzerland and Britain and the "abstention" of Germany. He, consequently, in estimating the progress of the chemical arts, recognises merely what was to be seen in Champ-de-Mars.

Preliminary Study on a Bridge over the Straits of Dover.—MM. Schneider and Hersent.—The total cost of this gigantic undertaking—which is not open to the grave objections existing against the proposed tunnel—is estimated at 860 million francs.

Fractionation of Simple Bodies.—An abridgment of the Presidential Address of Mr. Crookes, delivered before the Chemical Society in March, 1889.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 51.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

- MONDAY, June 2nd.—Society of Chemical Industry, 8. "Some Considerations on the Chemistry of Hypochlorite Bleaching," by Messrs. Cross and Bevan.
Royal Institution, 3. General Monthly Meeting.
TUESDAY, 3rd.—Royal Institution, 3. "The Natural History of Society," by Andrew Lang.
Institute of Civil Engineers, 8. (Anniversary).
WEDNESDAY, 4th.—Geological, 8.
THURSDAY, 5th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
Chemical, 8. "Note on the Preparation of Pure Crystalline Copper," by C. C. Duncan.
Royal, 4.30.
FRIDAY, 6th.—Royal Institution 9. "The Search for Coal in the South of England," by Prof. W. Boyd Dawkins, M.A., F.R.S.
Physical, 8. "The Effect of Change of Temperature on the Villari Critical Point of Iron," by Herbert Tomlinson, F.R.S. "The Diurnal Variation of the Magnet at Kew," by W. G. Robson and S. W. Smith.
Geologists' Association, 8.
SATURDAY, 7th.—Royal Institution, 3. "The Ballad Music of the West of England" (with musical illustrations), by Rev. S. Baring-Gould, M.A.

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THE CHEMICAL NEWS.

Vol. LXI. No. 1593.

NOTES ON VALENCY, BASICITY, COMPLEX ACIDS, AND CHEMICAL NOTATION.

By T. STERRY HUNT.

1. In the now obsolescent electro-chemical hypothesis of Berzelius certain chemical relations between different elements or their oxygen or sulphur compounds were distinguished by the terms electro-negative and electro-positive, or by the corresponding signs of *minus* and *plus* ($-$ $+$). As synonymous with these the names of acidic and basic or basylous, or of chlorous and zincous, have been employed. While none of these terms are free from objections, we may perhaps employ the words negative and positive (without the Berzelian prefix), while occasionally making use of acidic and basylous as synonymous with them when speaking of oxidised compounds.

2. When, in accordance with the discovery of Newlands, the chemical elements are arranged in successive series according to their equivalent weights and their valency, and when, moreover, as shown by Mendeleeff in his table of the periodic law, the even and the odd series of the first seven groups are each divided into two sub-groups, it is very apparent, as pointed out by the latter chemist, that the elements in most of the odd series of these seven groups are more markedly negative than those of the corresponding even series. If we except the second series, which is anomalous in other respects, we note evidences of this predominance of negative relations in the odd sub-groups of VIII.*b* in Cl Br I, of VI.*b* in S Se Te of V.*b* in P As Sb, of IV.*b* in Si Ge Sn Pb, and of III.*b* in Al Ga In.

Farther inspection, moreover, shows that in passing from the second series, in which the relations of negative and positive between the two sub-groups are, as it were, confounded, a loss of negative and a gain of positive characters appears as we proceed to higher series. Thus, in II.*a* the comparatively feeble positive relations of the oxide of Be led Berzelius and others after him to regard it as a sesquioxide nearly related to alumina. It is, however, clearly a diad oxide, and is followed by those of Ca Sr Ba with increasing equivalent weights and augmented positive characters. Again, in II.*b* the action of heat on the hydrous chlorides of Mg and Zn shows these elements to be less positive than Cd, while the strongly basylous HgO not only decomposes a solution of ZnCl₂, but separates potassium hydroxide from a solution of KI to form a double potassio-mercuric iodide. In III.*a* the negative B is followed by the positive Sc, and by Tl La and Yb, which are strongly basylous. In III.*b* Al₂O₃ is at once negative to oxides of groups I. and II., with which it forms compounds known as aluminates, and positive to the strongly negative or acidic oxides of groups V., VI., and VII., forming with them salts which, when soluble, are not very stable. The basylous or positive character augments progressively in Ga and In. In IV.*a* the strongly negative character, seen in CO₂, is less marked in TiO₂, and ZrO₂, while negative to many oxides, sustains to others positive relations, playing the part of a salifiable base. The positive character is still more marked in CeO₂, while ThO₂ is strongly basylous, its hydroxide, like those of Tl La Ba Ca and Cd, absorbing carbonic dioxide from the atmosphere. In V.*b*, where negative characters are strongly marked in the triad and pentad oxides of P and As, the triad oxide of Sb is feebly and that of Bi is strongly basylous. While in VI.*a* the hexad oxides of Cr, Mo, and W are more or less

strongly negative, that of U is positive. The negative energies of VI.*b* and VII.*b* progressively diminish with the increased equivalent weight, and in the former sub-group FeO₂ is already feebly basylous, uniting like Al₂O₃ both with positive and with negative oxides. Too little is yet known to permit similar comparisons in VIII., and I may perhaps offer exceptions, but for all the other groups it may be said that the positive or basylous energy varies directly and the negative or acidic energy inversely as the equivalent weight of the element.

3. Half a century since, when the doctrine of valency was unknown, all basylous oxides were divided into protoxides (or suboxides) on the one hand and sesquioxides on the other. At that time Ga, In, and Tl were undiscovered, and the sesquioxides were chiefly represented to the chemist by alumina and the corresponding oxides of Cr, Mn, and Fe, to which might be added the rare oxides of Bi and U, and also that of Be erroneously reckoned in the same category. Certain chemical analogies led Berzelius, to whom we owe our first accurate knowledge of zirconia, to regard it also as a sesquioxide, Zr₂O₃, and this view was henceforth generally accepted by chemists (with the exception of Gmelin, who wrote it ZrO), until the determination of the vapour-density of the volatile zirconia chloride showed that zirconia, like silica (which Berzelius made SiO₂), was to be regarded as a tetrad oxide, ZrO₂. In those days also Sc and Yb were yet unknown, and Y and La, together with the corresponding oxides of Ce and Di, were universally regarded as protoxides. Hence alumina, with the so-called peroxides of chromium, manganese, and iron, which replace it in alums (together with the rare beryllic and zirconic oxides), became to chemists the type of sesquioxides. The contrast between these and other basylous oxides was such as to influence strongly the chemical classification of natural silicates, into so many of which alumina enters. It was in accordance with these views, further impressed upon chemical mineralogy by the authority of Rammelsberg, that the writer attempted, in 1885, the division of all such silicates into three parts:—(1) protosilicates or non-aluminous silicates, like chrysolite; (2) protopersilicates or silicates of alumina, and protoxides like orthoclase; (3) persilicates or silicates of alumina without protoxides. At the same time the sesquioxides of Cr, Mn, and Fe were rightly and zirconic oxide wrongly regarded as in certain cases more or less completely replacing alumina. The oxide of beryllium was, however, reckoned as a protoxide.

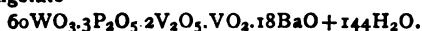
Apart from the erroneous position thus assigned to zirconia, the fallacy underlying this time-honoured distinction between protoxides and sesquioxides will be apparent when it is considered that it is not the sesquioxide or triad character of alumina which determines its relations in these silicates, and in other combinations, but its position intermediate between negative and positive triad oxides, which makes it acidic to monad and diad basylous oxides, on the one hand, and basylous to the more strongly negative oxides on the other. Alumina is positive to the negative pentad and hexad oxides, but its relations to SiO₂ demand further and special consideration.

4. Those silicates in which alumina occurs, together with other and more distinctly basylous oxides, are, in accordance with known chemical analogies, to be regarded as salts of a composite aluminosilicic acid, belonging to the class designated as "compound inorganic acids" by Wolcott Gibbs, whose generalisations on the subject constitute a most important contribution to theoretical chemistry. These composite mineral acids may be defined as combinations of two or more negative or acidic oxides, often of different groups, frequently attaining very high equivalent weights, and often of comparatively small saturating power. For the purposes of illustration it may be well to note some of these acids and their salts, in which we shall follow the notation adopted for them by Gibbs. The borotungstates of Klein are represented

respectively by $B_2O_3 \cdot 7WO_3 + 2R_2O$, $B_2O_3 \cdot 9WO_3 + 2R_2O$, $B_2O_3 \cdot 12WO_3 + 4R_2O$, and $B_2O_3 \cdot 14WO_3 + 3R_2O$. In the complex molybdates described by Struve and by Parmentier are two aluminomolybdates,—



besides corresponding chromic and ferric compounds and a manganomolybdate, $Mn_2O_3 \cdot 16MoO_3 + 5R_2O \cdot H_2O$. These same sesquioxides may also, according to Gibbs, unite at the same time both with phosphoric and molybdic oxides to form still more complex bodies. We have, moreover, silicotungstates, phosphotungstates, vanadotungstates, arsenotungstates, antimoniotungstates, and even stannophosphomolybdates and stannophosphotungstates of various degrees of complexity in which the negative or acidic member is made up of tetrad, pentad, and hexad oxides united. Besides the tetrad oxides SiO_2 and TiO_2 , other tetrad forms, as VO_2 , MoO_2 , and WO_2 , and moreover, in addition to the pentad oxides named, triad oxides of P and As. Portions of the oxygen in molybdic and tungstic hexad oxides may be replaced by fluorine, while hydrocarbon radicles like ethyl, methyl, and phenyl appear also to be capable of entering into these compounds. In the case of the silico-tungstates of Marignac, two types are known in which SiO_2 is united respectively with $10WO_3$ and $12WO_3$, while in the phosphotungstates, according to Gibbs, we have a homologous series, the extreme terms of which, so far as known, are $P_2O_5 \cdot 6WO_3 + 6H_2O$ and $P_2O_5 \cdot 24WO_3 + 6H_2O$, the common difference being $2WO_3$. As example of still greater complexity he gives us as the formula of a phosphotungstate—



All of the above described salts are soluble and crystallisable, while the anhydrous, dense, insoluble, and quasi-metallic tungsten-bronzes are regarded as salts of analogous constitution.*

The consideration of these salts of complex mineral acids will help us to understand better the problems presented by the native silicates, and their relations to boric and aluminic oxides on the one hand and to TiO_2 , the various pentad and hexad oxides, and fluorine and chlorine on the other. The analogies of the borotungstates and the aluminotungstates lead us to admit the existence of borosilicates, boralaminosilicates, and aluminosilicates in which the oxides of boron, aluminum, and silicon alike play the part of negative or acidic elements. The importance of clearly defining these relations is rendered more evident by the fact that over one-half of all the native silicates known to mineralogy (without counting the small number of simple aluminosilicates, hydrous and anhydrous) contain alumina together with some more distinctly basylous oxide. The sesquioxides of Cr, Mn, and Fe (and even of Ti) may occasionally replace alumina, not in virtue of their triad constitution, but because of their relatively negative characters, which bring them near to it chemically. It will be found that the markedly basylous triad oxide, like those of Y, La, Ce, and Di, do not replace Al_2O_3 , but, on the contrary, take the place of diad oxides.

5. Among native oxidised aluminous species, besides the compounds of alumina with pentad and hexad oxides, may be distinguished:—(1) *Aluminates*, including non-silicified compounds of negative alumina with other more basylous oxides; (2) *Aluminosilicates* in which a complex aluminosilicic acid is combined with one or more basylous or positive oxides; (3) Simple silicates of alumina into which Al_2O_3 may be supposed to enter, as in its phosphates and sulphates, as a positive or basylous element, but which it may also be permitted to regard as generated by the more or less complete elimination of H_2O from normal aluminosilicic hydrates, which are thereby at last converted into anhydride of these complex acids.

An examination alike of the variations in the relative proportions of alumina and silica, and in the basicity of the native aluminosilicates soon suffices to show that a great multiplication of formulæ would be necessary to include all the known types, and furthermore, that attempts to unite them with Al_2O_3 and SiO_2 would make their notation inconveniently cumbersome. While the constitution of these aluminosilicates is probably as complex as that of any of the borotungstates, aluminomolybdates, silicotungstates, phosphomolybdates, and phosphotungstates already noticed, it has long seemed desirable to the writer to devise for these silicates and for mineral species in general a notation as near as may be monadic, and one in which the valencies alike of negative and positive elements should be made apparent. These ends it is sought to attain by employing for all monads and diads the ordinary chemical symbols in small ordinary roman letters; for all triads and for the hexad uranic oxide, small italic letters; and for all tetrads, small black-faced roman letters. Those elements which yield basylous oxides at once monad and diad or triad, are distinguished in their monad forms by duplicating the initial letter, as ccu, hhg, aau, ttl. The equivalent weight of diads is divided by 2, that of triads by 3, and that of tetrads by 4, to correspond in each case with monadic oxygen = $O \div 2 = o = 8$, and with monadic fluorine = $f = 19$. For the pentad and hexad negative oxides, however, we employ diad symbols, conjoined, however, with monad oxygen. The symbols of the elements are in all cases followed by the coefficient, even though this should be unity.

In illustration of this system as applied to certain well-known aluminosilicates, we give the ordinary and the monadic notations side by side.

Anorthite ..	$Al_2O_3 \cdot 2SiO_2 + MO = al_3o_3si_4o_4$	$al_3o_3si_4o_4$
Leucite ..	$Al_2O_3 \cdot 4SiO_2 + MO = al_3o_3si_8o_8$	$al_3o_3si_8o_8$
Albite ..	$Al_2O_3 \cdot 6SiO_2 + MO = al_3o_3si_{12}o_{12}$	$al_3o_3si_{12}o_{12}$
Meionite ..	$3Al_2O_3 \cdot 6SiO_2 + 4MO = al_9o_9si_{12}o_{12}$	$al_9o_9si_{12}o_{12}$
Garnet ..	$Al_2O_3 \cdot 3SiO_2 + 3MO = al_3o_3si_6o_6$	$al_3o_3si_6o_6$
Zoisite ..	$4Al_2O_3 \cdot 9SiO_2 + 6MO = al_{12}o_{12}si_9o_9$	$al_{12}o_{12}si_9o_9$

These monadic formulæ may be further condensed by uniting in one term the oxygen of the different oxides. Albite will then become $al_3si_{12}m_{12}o_{12}$, and meionite $al_9si_{12}m_{12}o_{12}$. In this notation andalusite and cyanite are $al_3si_2o_5$, and topaz $al_3si_2(o_4f_1)$. The new formulæ, in which m = a monadic portion of a monad or a diad base, corresponding to 8 parts of oxygen, will suffice to show the simplicity of the monadic notation here proposed, which gives at once the oxygen ratios, and distinguishes between the monads and diads on the one hand and the triads and the tetrads on the other. The numerical value calculated for the formula ($o_1 = 8$) divided by the sum of the oxygen coefficients gives the mean value = gravity = d (water being unity) gives the reciprocal of the coefficient of condensation of the species = N. This datum enables us to compare different species as to their relative condensation, upon which, as we have elsewhere shown, their hardness and their chemical indifference depend.

New York, April 27, 1890.

ON THE PRESENT CONDITION OF THE PHILADELPHIA WATER SUPPLY.†

By SAMUEL C. HOOKER.

SINCE my third report was presented to this Society a great deal of space has been devoted in the daily papers

* Such a notation, with the exception of the use of unlike letters for diads, triads, and tetrads, was employed by the writer in 1885 in his essay on "The Classification of Silicates, Mineralogy, &c.," pp. 320–370.

† Proceedings of the Chemical Section of the Franklin Institute, May, 1890.

to the discussion of our water supply, and while one cannot but regret that much has been said which is both exaggerated and untrue, it is a matter for congratulation that the subject has once again been brought prominently before the public.

During a large portion of last summer, the water supplied to all parts of the city, without exception, was almost uninterruptedly muddy. Under these circumstances it is scarcely to be wondered that there should have been a disposition to make the worst of a condition of affairs certainly bad enough without the least exaggeration. It is too much to expect that the newspaper should possess in all or even in most cases the necessary knowledge to discriminate between facts which have and others which have no weight, between arguments and opinions which are or are not entitled to consideration, and the result has been that an immense amount of misleading information, a vast number of positively incorrect and worse than valueless statements have been distributed broadcast to the public. Facts have been dwelt upon which have no weight, self-constituted authorities have been quoted whose statements have been remarkable for their inaccuracy, positively ridiculous for their scientific absurdity.

While, however, there has been unquestionable exaggeration in the arguments used against the water, there has also been a deplorable exhibition of bias and misinformation, and a positive disinclination to admit facts on the part of certain gentlemen, who appear to regard the present condition of our water supply as all that can be desired.

For three months, after the publication of my third report, I continued the laborious investigation, the early results of which have been already communicated to you. The publication of the numerous analyses has, however, been purposely delayed, because it was thought probable that they would be more fairly and impartially considered after the excitement created by the newspaper agitation had subsided. My analyses did not justify me in speaking as badly of the water as several of the newspapers were able to do, and any less vehement protest against its condition would have failed at that time to have attracted the attention which I hope will now be given to this paper.

In the following Table will be found, as the condensed result of my investigation, average figures for the water collected at different parts of the city during six months of last year:—

Samples collected March to September, 1889.	Chlorine.	Free ammonia.	Albumenoid ammonia.	Nitrogen of nitrates.
West Philadelphia, Forty-fourth and Chestnut Streets (24 samples) ..	0.233	0.0015	0.0080	0.099
Sixteenth and Locust Streets (23 samples) ..	0.254	0.0014	0.0081	0.098
Twentieth Street and Columbia Avenue (23 samples) ..	0.266	0.0024	0.0097	0.100
Front and Bainbridge Streets (23 samples) ..	0.265	0.0013	0.0076	0.099
Average of 99 city samples ..	0.254	0.0016	0.0083	0.099

For purposes were taken from some idea might be formed of the extent of the pollution occurring within about 25 miles of the city. The samples from Phoenixville were furnished to me through the courtesy of the Water Department. For the other samples I am indebted to the kindness of several gentle-

men residing in the various neighbourhoods in which they were collected, who most cheerfully undertook the troublesome task of drawing the water for analysis at stated times.

Deferring for a moment the consideration of the Phoenixville samples, and judging the water by such standards as are universally adopted, when the history of the water examined is entirely unknown, we are compelled to acknowledge that the above analyses do not in any way condemn the water, but, on the contrary, we must admit that the chlorine, free and albumenoid ammonias, and the nitrates are present in quantities less than they are known to exist in many absolutely unpolluted waters.

By comparing the water at Phoenixville, however, with that supplied for city use, we are able to detect in the city water a slight increase in the quantity of the substances estimated, indicating that the sewage pollution, which we know exists, has occurred to an extent sufficient to appreciably influence the composition of the water.

The following Table gives the average results of analyses of five samples of water obtained from each of the points named at nearly corresponding dates:—

	Chlorine.	Free ammonia.	Albumenoid ammonia.	Nitrogen of nitrates.
Phoenixville (average of 5 samples)	0.196	0.0039	0.0079	0.084
West Philadelphia, Forty-fourth and Chestnut Streets (average of 5 samples) ..	0.227	0.0022	0.0101	0.085
Sixteenth and Locust Streets (average of 5 samples)	0.264	0.0017	0.0099	0.088
Twentieth Street and Columbia Avenue (average of 5 samples) ..	0.242	0.0027	0.0126	0.086
Front and Bainbridge Streets (average of 5 samples) ..	0.260	0.0012	0.0078	0.083

Passing on to the discussion of each of the impurities determined, we may at once dismiss the nitrates from consideration, as the quantities present in the various samples of water examined differed only slightly from each other. It will be observed that the chlorine in the water drawn at all points in the city is greater than that found in the samples from Phoenixville.

Similarly, the albumenoid ammonia in three out of the four localities in the city is distinctly greater than in corresponding samples from Phoenixville. With regard to the free ammonia a decrease in quantity is observed in the city water, but in spite of this, in view of the figures for albumenoid ammonia, we are compelled to regard the quantity of the organic substances discharged into the river after leaving Phoenixville as somewhat greater than the combined action of the natural processes of purification and the subsiding reservoirs has been able to dispose of. During the six months covered by my investigation these impurities were almost entirely mechanically suspended, and by a suitable system of filtration could have been readily removed, leaving the water remarkably free from organic matter.

That most of the organic substances reaching the city should be pumped from the river in an insoluble form is not, after all, extraordinary. A considerable proportion of the organic matter of sewage exists, of course, in solution, but as many varieties of waste from as many factories, &c., are discharged into the river, it is probable that these substances, by acting and reacting on each other, give rise to the formation of precipitates, which in some cases may consist essentially of organic matters formerly in solution, in others which may mechanically enclose them. However this may be, the fact remains

that the organic matter of the Schuylkill water, during the six months of last year that I investigated the subject, was almost and entirely in suspension and the condition of the water, deprived of its suspended matters, was entirely satisfactory, and often of a very high degree of purity.

Mud, whether wholesome or unwholesome, has obviously no place either in drinking water or in water to be used for household or industrial purposes, and to show, therefore, that the mud of the Schuylkill water is accompanied by precipitated organic matters derived from sewage, seems to me to add little to the many emphatic arguments which can be already urged with unquestionable force against its presence being tolerated. But, on the other hand, by showing that practically the entire amount of the substances which can be considered objectionable are present in suspension and can be readily removed, leaving a water of a high degree of purity, how strong an argument we have for carrying out such purification.

In order that Schuylkill water may be filtered satisfactorily on a large scale, it is necessary to use a so-called "coagulant," and whether this be alum or iron, it is probable that the result will be much the same. Economical and mechanical considerations will have to be carefully weighed in choosing between them. The beneficial action of both these substances depends upon the formation of precipitates, which, in the act of separation, entrap and enclose the microbes and suspended particles, so that they can be arrested during subsequent filtration through sand. If the filtration be attempted without the addition of the coagulant, the very minute particles to which the turbidity of the water is due pass through the interstices of the filter-bed unchecked, but by first entrapping them in the precipitates derived from the coagulant used, they are virtually increased in size and can be arrested by the sand bed.

There is so much prejudice against alum that it is desirable to discuss its use in the purification of water somewhat in detail. Alum is a double sulphate of aluminium and potassium, and contains a large proportion of water of crystallisation. Its percentage composition is as follows:—

Sulphate of aluminium	36.07
Sulphate of potash	18.35
Water of crystallisation	45.58
	100.00

The sulphate of aluminium is the active portion of the alum and may be substituted for it if desired.

As soon as the alum is added to the water the carbonates present in solution react with the sulphate of aluminium, becoming themselves converted into sulphates with the formation of unstable carbonate of aluminium. The latter gives off carbonic acid gas and alumina separates. It is evident, therefore, that the separation of the alumina is not attended by the formation of free sulphuric acid, as has been alleged. The addition of alum to the water slightly increases the quantity of sulphates present, and a small quantity of carbonate of lime is usually converted into sulphate of lime. The aluminium is entirely precipitated as alumina, and unless a considerable excess has been used, none whatever remains in solution.

I have dwelt upon the action of alum at so great a length (1) because I have been much impressed by the results which can be obtained by its use; (2) because it forms an essential feature of the American system of filtration; and (3) because I am convinced that the objections which have been urged against it are based upon an erroneous conception of its mode of action.

If it is the presence of microbes which is to be mainly feared in drinking-water, there can be, aside from boiling the water, no surer way of getting rid of them than by

the use of a coagulant. The efficiency of iron for this purpose has been amply demonstrated at Antwerp and elsewhere; and in the United States, Dr. Prudden, a well-known bacteriologist, of New York, has stated that he has found water purified by sand and alum filtration practically sterile. It has been frequently stated that microbes cannot be removed by filtration, that they will even pass a thousand abreast through the interstices of an ordinary sand-bed. In answer to this it may be said that while it is useless to look for good results by simple filtration at any speed which may be considered practical through clean sand alone, the matter is entirely changed by the use of a coagulant, and the smaller the particles, the more minute the microbes, the more surely are they entrapped in, surrounded, and held by the precipitate formed.

The albumenoid ammonia in Schuylkill water, purified by sand and alum, has been often determined in my laboratory, and has always fallen below 0.0050 part per 100,000.

There is scarcely a day when the water of Philadelphia does not reflect discreditably upon the city, its officials, and its citizens. If we had but the one alternative, the use of the Schuylkill in its present condition or the expenditure of 20,000,000 dols. to get water from elsewhere, we might possibly be excused for hesitation. But there are other ways of solving the difficulty. Water, considerably worse than that taken from the Schuylkill, has been successfully purified elsewhere, and why should not Philadelphia adopt a similar system of purification. It is evident that additional subsiding basins alone are impracticable for the work required. The enormous East Park reservoirs and the comparatively small amount of work they accomplish must have convinced all who have impartially considered the matter that some other method of purification must be adopted. The suspended matters of the Schuylkill water are mostly so minute and are deposited so slowly that very many times our present storage capacity would be necessary to render the condition of the water at all times uniformly clear and satisfactory. The large number and large size of the reservoirs required to do this and the immense outlay which their construction would involve would seem to be sufficient reason for looking to other methods of purification.

In conclusion, I desire to acknowledge my indebtedness to a gentleman who wishes to be nameless, not only for the interest he has taken in the progress of this investigation, but also for liberally sharing the expenses connected with it.

SOME POINTS IN THE DETERMINATION OF SILICA IN SILICATES BY FUSION WITH ALKALINE CARBONATES.*

By JAMES P. GILBERT, S.D.

THE usual method of determining silica in silicates—that of fusion with the alkaline carbonates, decomposition with hydrochloric acid, and subsequent evaporation to dryness—does not always give satisfactory results. This method is universally described in the text-books as being accurate, with the occasional caution that the filtrate should also be examined for any silica which may not have been rendered insoluble by evaporation to dryness. But one looks in vain for any intimation of what may be the amount of the error in the determination of silica as usually carried out if one neglects to examine the filtrate. There is no doubt that many chemists have had trouble with this method, and some have given it up, preferring to volatilise the silica with hydrofluoric and sulphuric acids, and, after a careful analysis of the residue, to calculate the silica by difference. A recent writer† makes the statement that he

* *Technology Quarterly*, vol. iii., No. 1.

† *George Craig, Chem. News*, vol. lx., No. 1563.

TABLE I.

Analyses of Blast-Furnace Slag (containing 46 per cent lime) by Fusion with Alkaline Carbonates.

	I.	II.	III.	IV.
	Residue insoluble in hydrochloric acid after evaporation to dryness. Per cent.	Weight of residue obtained from treating Column I. with hydrofluoric acid. Grm.	Weight of silica found in alumina. Grm.	Total silica. Per cent.
1.	41'25	0'0003	0'0006	41'26
2.	41'34	0'0024	0'0008	41'17
3.	41'39	0'0012	0'0009	41'33
4.	41'32	0'0020	0'0003	41'18
5.	41'22	0'0012	0'0009	41'19
6.	41'43	0'0021	0'0007	41'23
7.	41'40	0'0014	0'0009	41'32
8.	41'48	0'0017	0'0008	41'35
9.	41'33	0'0013	0'0005	41'25
10.	41'71	0'0036	0'0007	41'42
11.	41'53	0'0028	0'0007	41'27
12.	41'89	0'0031	0'0004	41'35
13.	41'79	0'0032	0'0002	41'41
14.	41'65	0'0027	0'0005	41'43
15.	41'90	0'0028	0'0001	41'48

Nos. 1 to 3 inclusive were dehydrated on the water-bath.

Nos. 4 to 6 inclusive were dehydrated at 125° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate over Bunsen burner.

Nos. 10 to 15 inclusive were dehydrated in air-chamber at 280° C.

All evaporations were made in porcelain.

TABLE II.

Analyses of a Blast-Furnace Slag (containing 35 per cent lime and 15 per cent magnesia).

	I.	II.	III.	IV.
1.	33'65	0'0032	0'0032	33'61
2.	33'90	0'0014	0'0025	33'18
3.	33'46	0'0013	0'0013	33'29
4.	33'71	0'0027	0'0004	33'40
5.	33'42	0'0021	0'0008	33'24
6.	33'75	0'0031	0'0004	33'36
7.	33'49	0'0032	0'0011	33'24
8.	33'85	0'0045	0'0012	33'27
9.	33'90	0'0042	0'0012	33'30
10.	33'65	0'0062	0'0062	33'62
11.	33'83	0'0046	0'0045	33'80
12.	33'95	0'0088	0'0050	33'60

Nos. 1 to 3 inclusive were dehydrated on the water-bath.

Nos. 4 to 6 inclusive were dehydrated at 120° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate over Bunsen burner.

Nos. 10 to 12 inclusive were dehydrated at 280° C.

TABLE III.—Analyses of a Sample of Orthoclase.

	I.	II.	III.	IV.
1.	64'80	0'0018	0'0004	64'52
2.	64'13	0'0018	0'0030	64'30
3.	64'03	0'0026	0'0035	64'20
4.	64'35	0'0020	0'0030	64'52
5.	64'98	0'0050	0'0019	64'45
6.	64'62	0'0035	0'0020	64'36
7.	64'83	0'0068	0'0030	64'45
8.	64'27	0'0083	0'0039	64'35

Nos. 1 and 2 were dehydrated on the water-bath.

Nos. 3 and 4 were dehydrated at 120° C.

Nos. 5 and 6 were dehydrated on iron plate over Bunsen burner.

Nos. 7 and 8 were dehydrated at 280° C.

has never been able to obtain more than 97·5 per cent of the total silica in highly siliceous bodies by the fusion method. The following work was undertaken in the hope of discovering some of the sources of error in the fusion process.

The influence of the temperature at which the silica is dehydrated was first investigated. Most authorities say that evaporation on the water-bath to complete dryness, or until no more hydrochloric acid is given off, is sufficient to dehydrate the silica, but a few recommend subsequent heating in an air-chamber to a temperature of 110° C. A higher temperature than 110° C. is said by Fresenius to be inadmissible, since there is liability of the silica re-combining with the bases present to form silicates partially decomposable with hydrochloric acid.

To test the influence of temperature on the amount of silica obtained, the following determinations of silica were made in a blast-furnace slag containing about 46 per cent of lime, 10 per cent of alumina, and less than 1 per cent of magnesia. The silica was dehydrated at various temperatures, but in all other respects the process was carried out exactly as Fresenius directs. What is generally called silica, that is, the mass insoluble in hot hydrochloric acid after evaporation to dryness, is given in Column I. of Table I. This was treated with hydrofluoric acid, and the weight of the residue is given in Column II. In the filtrate from the silica the alumina was precipitated by ammonia, dried, ignited, and then fused with potassium bisulphate. The residue left on treating the fused mass with water (and correcting for the impurities of the bisulphate used) is given in Column III. The total silica in Column IV. is calculated by subtracting the weight of the residue left after treatment with hydrofluoric acid from the weight of the silica as given in Column I., and adding that found with the alumina in Column III.

In this series of results it will be seen that the silica was practically all rendered insoluble even at the temperature of the water-bath, and that there was no gain in this respect in using a higher temperature. But the amount of foreign matter in the silica was, in general, perceptibly higher at the higher temperature of dehydration. This is probably due to the alumina being rendered partially insoluble in acid. From the fact that very little silica was found in the alumina, it would seem as if there were no tendency for the silica to re-combine with the lime and alumina even at a temperature of 280° C. Nos. 13, 14, and 15 were digested, after dehydration, with hot acid for one hour, in the expectation of dissolving out all the alumina and other bases, but this treatment did not give smaller residues after the volatilisation of the silica with hydrofluoric acid than in Nos. 10, 11, and 12, which were treated only thirty minutes with acid.

The general uniformity of the results in this series suggested the possible influence of the calcium chloride present in dehydrating the silica on evaporation to dryness. This led to the second point considered, namely, the influence of the salts present on the determination of silica. It is not unreasonable to suppose that some salts, such as calcium chloride, may have a beneficial influence, while others, as, for example, magnesium chloride, which is decomposed when its solution is evaporated, may vitiate the silica determination by forming a silicate which will be subsequently decomposed by hydrochloric acid with solution of the silica. To test the effect of magnesium chloride, determinations of silica were made in a slag containing about 35 per cent of lime, 15 per cent of magnesia, and 15 per cent of alumina. (See Table II.).

This series differs from the first mainly in the large amount of impurity in the silica and the large amount of silica in the alumina when the dehydration is effected at a temperature of 280° C. The best results were obtained at a temperature of 120° C. The increase of silica in the alumina as the temperature is increased would seem to be due to the magnesia, for the conditions were, in all other respects, the same as in the analyses of the other slag. The above results indicate that there is no danger

of the silica combining with the magnesia at 120°C ., and that at this temperature the silica is almost completely dehydrated, the calcium chloride probably assisting in the dehydration.

A series of analyses was next made on orthoclase, practically free from lime and magnesia. (See Table III.).

This series differs from the previous one in that the higher temperature is not accompanied with an increased amount of silica in the filtrate. This would seem to be a confirmation of the idea that there was a re-combination of the silica and the magnesia at the temperature of 280°C . in the magnesia slag; and the fact that the amounts of silica found in the alumina are (with one exception) uniformly higher than those in the lime slag indicates, I think, the beneficial effect of the calcium chloride in the dehydration of the silica.

The third point considered was the influence of temperature on the dehydration of the silica when no bases other than the alkalis were present. From the last three series of analyses it would seem that some silica always fails to be rendered insoluble by heat alone, so that, if a definite amount of pure silica were taken and subjected to alternate fusions and dehydrations, we should expect that the amount of silica obtained would diminish at each successive treatment. To ascertain if this were so, two determinations of silica were made in the lime slag, and the silica thus obtained repeatedly treated by fusion with alkaline carbonates in the usual way. The per cent of silica recovered in each case is given below. The silica obtained from the slag by the first fusion and dehydration is taken as 100 per cent.

	I. Per cent.	II. Per cent.	
1.	42.02	41.81	Silica in slag obtained by heating to 280°C . Percentage of the above obtained in four successive fusions by heating to 120°C .
2.	97.24	97.79	
3.	96.04	96.70	
4.	95.17	95.96	
5.	94.19	95.45	

The large difference between the results of the first and second fusions is probably due to impurities in the silica, which was heated to 280°C .; but the variations in the other cases can only be due to loss of silica by incomplete dehydration. Still, these are better results than Craig obtained, who does not, however, mention the temperature he used in dehydrating the silica.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 15th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MR. JAMES HAMILTON was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Charles F. Branson, Kenley Lodge, Macaulay Road, Clapham Common; John Hutchinson Edward, 117, Stockport Road, Manchester; Arthur R. Haslam, Ph.D., 64, Rathgar Road, Dublin; John Robert Johnson, 16, Oxford Street, Liverpool; Patrick Kelly, 43, Lennox Street, Dublin; Thomas Parker, M.I.C.E., Wolverhampton; Richard James Redding, Royal Laboratory, Woolwich Arsenal; Frederick Smith, Johannesburg, Transvaal, South Africa.

The following were elected Fellows of the Society:—James Robert Appleyard; William Henry Blake; James

Kear Colwell; S. Sydney Monckton Copeman, M.A., M.B.; Andrew Fairgrieve; G. H. Finlay; John Archyhl Jones; Oliver Kirk; Robert Walter Oddy; William Tate.

The following papers were read:—

36. "*Diethylphosphorous Acid*." By T. E. THORPE, F.R.S., and BARKER NORTH, Associate of the Normal School of Science.

The authors describe the mode of preparing this compound and its properties. It is obtained by adding alcohol, drop by drop, to phosphorous oxide contained in a vessel surrounded with ice and salt. It is a colourless mobile liquid, possessing a peculiar penetrating alliaceous smell. Its vapour is poisonous, and even small quantities produce headache and nausea. It boils at 184 – 185° , and has the relative density 1.0749 at—

15.5° .

4

It interacts with water, forming alcohol and phosphorous acid, and is converted by bromine into ethyl bromide and metaphosphoric acid.

37. "*The Homonuclear Trichloronaphthalenes*." By HENRY E. ARMSTRONG and W. P. WYNNE.

1 : 2 : 3-*Trichloronaphthalene*.—The compound prepared by Faust and Saame from α -chloronaphthalene tetrachloride has been shown by Widman to be this modification, the proof being that it affords nitrotrichlorophthalic acid on oxidation with nitric acid; the authors have obtained it from a novel source—by the action of phosphorus pentachloride on Zincke and Kegel's α -dichloro- β -naphthol (*Berichte*, 1888, 3385). This naphthol derivative is found to crystallise in aggregates, such as Zincke and Kegel describe, of long prismatic needles springing from a common centre—m. p. 76 – 77° ; also (a) in fairly large aggregates composed of characteristic short stumpy prisms—m. p. 76 – 77° ; and (b) in very long, slender, flat, transparent needles melting at 66° and, on re-fusion, at 74° . In no case was a higher melting-point than 77° observed. Zincke and Kegel, however, give 81° as the melting-point of the substance; and it is noteworthy, therefore, that the authors find the melting-point of trichloroketonaphthalene to be 92 – 93° , instead of 96° , and that one of them, in conjunction with Mr. Rossier, has found that the various chloro-derivatives of β -naphthol described by Zincke and Kegel uniformly melt at temperatures about 4° lower than stated by these chemists; it may also be mentioned that a similar discrepancy is to be noted in the case of a recent paper of Clausius (*Berichte*, 1890, 517), who specially calls attention to the fact that he finds the melting-point of 2 : 2'-dihydroxynaphthalene to be 4° higher than previously observed.

$\alpha\beta$ -Dichloro- β -naphthol exchanges its hydroxyl for chlorine when distilled with the theoretical quantity of phosphorus pentachloride at 240 – 250° . The resulting trichloronaphthalene crystallises from alcohol, in which it is sparingly soluble in the cold, either in long, very slender needles or in radiate aggregates of flat needles; it melts at 81° . It is but little acted on when heated at 100° with H_2SO_4 , but is readily sulphonated when digested at 100° for an hour with four times its weight of acid containing 10 per cent SO_3 . The barium salt of the acid, $(\text{C}_{10}\text{H}_4\text{Cl}_3\text{SO}_3)_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$, crystallises in small spherical aggregates, and is sparingly soluble in water; the potassium salt, $\text{C}_{10}\text{H}_4\text{Cl}_3\text{SO}_3\text{K}$, is very soluble in water, but sparingly soluble in alcohol, from which it crystallises in minute anhydrous needles. The chloride,—



crystallises from benzene, in which it is very soluble, in small prismatic needles; from petroleum spirit, in which it is sparingly soluble, in small, flat, slender needles; and from acetic acid in white aggregates of very small needles; it melts at 182° . The amide could not be obtained crystalline; it melts at 296° . The chloride was hydrolysed by prolonged heating with concentrated muriatic

acid at 260°; the regenerated trichloronaphthalene crystallised from alcohol in long slender needles melting at 81°.

1:2:4-Trichloronaphthalene.—This modification was first prepared by Cleve, who most accurately described its properties (*Berichte*, 1888, 893), from dichloralphanaphthol; the authors prefer to prepare it from dichloralphanaphthylamine. It melts at 92°. When sulphonated, either by means of the theoretical quantity of SO_3HCl or by heating with twice its weight of H_2SO_4 at 100° for one hour, it yields an acid which, when dissolved in water, forms a viscid solution—in this respect resembling the acid obtained by sulphonating 1:4-dichloronaphthalene. The barium salt of the acid, $(\text{C}_{10}\text{H}_4\text{Cl}_3\text{SO}_3)_2\text{Ba} + 3\text{H}_2\text{O}$, is very sparingly soluble in water, and crystallises in fluffy masses of very small slender needles; the potassium salt $\text{C}_{10}\text{H}_4\text{Cl}_3\text{SO}_3\text{K}$ is extremely soluble in water, but sparingly soluble in alcohol, from which it crystallises in anhydrous, short, slender needles. The chloride $\text{C}_{10}\text{H}_4\text{Cl}_3\text{SO}_2\text{Cl}$ crystallises from benzene in tufts of long slender needles; from petroleum spirit, in which it is sparingly soluble, in long slender needles; and from acetic acid in slender flat needles; it melts at 157–158°. The amide crystallises from alcohol in tufts of short slender needles, and melts at 235°. The chloride was hydrolysed with considerable difficulty, requiring prolonged heating at 260–265° with concentrated muriatic acid; the resulting trichloronaphthalene crystallised from alcohol in tufts of slender flat needles melting at 92°.

38. "The Ten Isomeric Dichloronaphthalenes and the Sulphonic Acids and Trichloronaphthalenes Derived therefrom." By HENRY E. ARMSTRONG and W. P. WYNNE.

Whereas theoretically only ten dichloronaphthalenes are possible, twelve have actually been described. Nine of these are already proved to be definite substances, and their constitution may be regarded as well established (*Proc. Chem. Soc.*, 1888, 104; 1889, 34, 48); these nine include the three possible $\alpha\alpha$ -, the four possible $\alpha\beta$ -, and the two possible hetero- $\beta\beta$ compounds. Of the remaining three, one—the so-called α -dichloronaphthalene (m. p. 38°)—has been shown by the authors to be non-existent, and to consist of the 1:3- (m. p. 61°) and 1:4- (m. p. 68°) modifications (*Proc. Chem. Soc.*, 1888, 106). A second is undoubtedly also non-existent, viz., the " κ -dichloronaphthalene" (m. p. 94°), which, according to Claus (*Ber.*, 1882, 314) is obtained by the action of phosphorus pentachloride on the α -naphtholsulphonic acid prepared by sulphonating α -naphthol dissolved in acetic acid. The several monosulphonic acids formed from α -naphthol, however, correspond to one or other of the nine recognised dichloronaphthalenes, and on this ground alone the production of the tenth, and—it is to be supposed—only possible, modification in such a manner appears impossible, even if the fact be left out of account that homo- $\beta\beta$ -dichloronaphthalene—the only modification required in addition to the nine above specified in order to complete the list—cannot be prepared from α -naphthol. α -Naphthol is converted, with exceptional facility, into the 1:2:4-disulphonic acid, and the corresponding trichloronaphthalene melts at 92°, which is very nearly the melting-point of Claus's compound; the authors, therefore, have little doubt that the substance described by Claus as κ -dichloronaphthalene was in reality 1:2:4-trichloronaphthalene.

The only remaining modification to be considered is the 1-dichloronaphthalene (m. p. 120°), first prepared by Leeds and Everhard by heating naphthalene tetrachloride with silver oxide, and which was subsequently separated by Widman from the product of the action of alcoholic potash on the tetrachloride. Until it was discovered that a dichloronaphthalene was a mixture of the 1:3 and 1:4 compound, the authors were inclined to think that perhaps this modification was impure 1-dichloronaphthalene (*B. A. Report*, 1888); but the necessity for this assumption, occasioned by the existence of the α -compound, having

been removed, it appeared highly probable that the α -compound was the homo- $\beta\beta$ -modification—and this proves to be the case, the authors having succeeded in obtaining a substance with all the properties ascribed by Leeds and Everhard and by Widman to 1-dichloronaphthalene by a novel method, which places its constitution beyond all doubt, viz., by partially reducing 1:2:3-trichloronaphthalene.

The existence of a complete series of ten isomeric dichloronaphthalenes may, therefore, now be regarded as established. No fewer than eight of these have been discovered by Cléve and his pupils; all who study the subject must be led to admire the work of the Swedish chemists, and to recognise the influence which it has exercised.

In order to characterise the various dichloronaphthalenes, and also to determine the manner in which constitution affects the course of chemical change in the case of naphthalene derivatives, the authors have sulphonated the ten modifications, and have converted the resulting sulpho-acids into trichloronaphthalenes. A brief account of the results is now given, details with reference to the composition of the salts, &c., being reserved for a full communication.

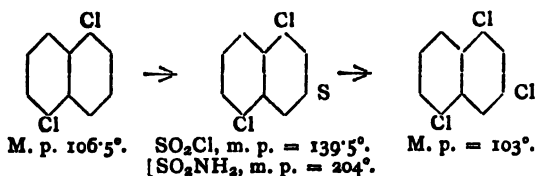
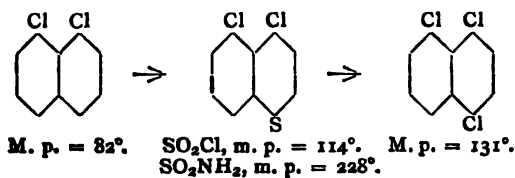
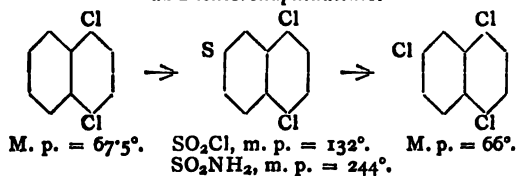
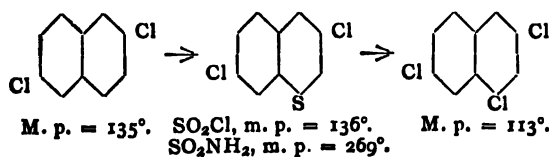
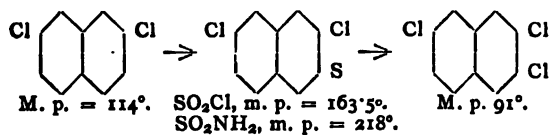
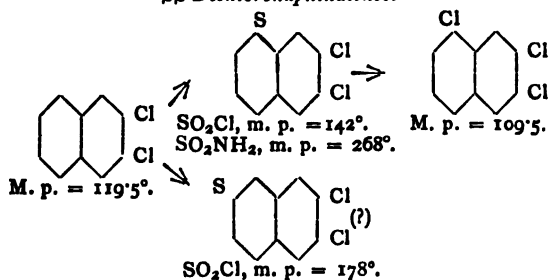
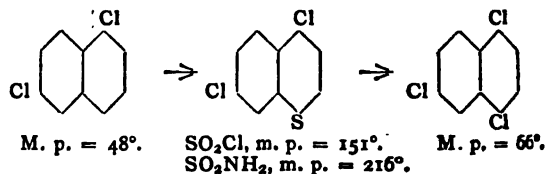
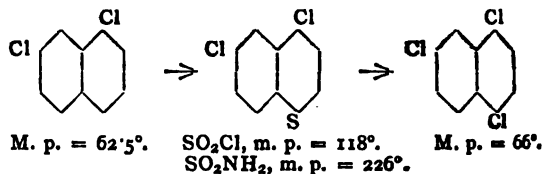
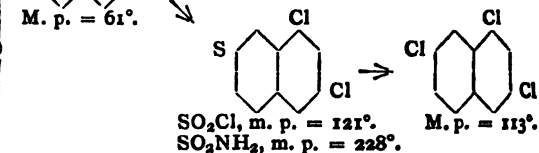
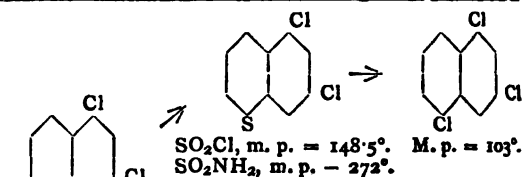
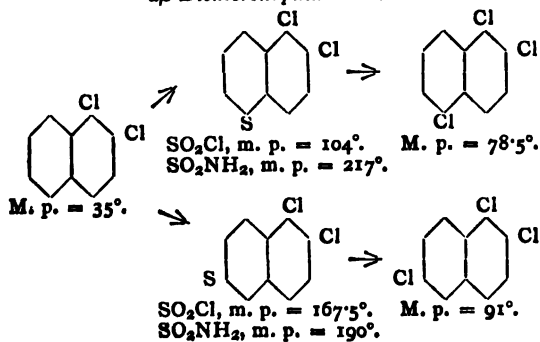
To avoid the possibility of the occurrence of secondary changes induced by the presence of water, chlorosulphonic acid was throughout employed as the sulphonating agent instead of sulphuric acid, and sulphonation was effected by adding slightly less than the theoretical quantity of this agent to a 10 per cent solution of the dichloronaphthalene in dry carbon bisulphide; the carbon bisulphide was subsequently removed by distillation on a water-bath, the acid dissolved in water, and the solution steam-distilled to free it from unattacked dichloronaphthalene and traces of carbon bisulphide, and finally filtered to remove the small proportion of insoluble non-volatile compound (sulphochloride or sulphone) always formed.

$\alpha\alpha$ -Dichloronaphthalenes.

1. 1:4-Dichloronaphthalene. — On sulphonation, this yields a practically uniform product, a very small proportion of an isomeric acid of undetermined constitution being simultaneously formed. The chloride of the acid, $\text{C}_{10}\text{H}_4\text{Cl}_2\text{SO}_2\text{Cl}$, crystallises from benzene in aggregates of slender prismatic needles melting at 132°, identical with the chloride of Widman's dichloronaphthalene- β -sulphonic acid; the amide is sparingly soluble in cold alcohol, and crystallises in tufts of very slender long needles melting at 244°. The corresponding trichloronaphthalene crystallises in tufts of slender needles, which, on standing, undergo conversion into opaque, white aggregates melting at 66° (*Proc. Chem. Soc.*, 1890, 18). The sulphochloride undergoes hydrolysis when heated with concentrated muriatic acid at 260–265°; the pure dichloronaphthalene thus obtained crystallises from alcohol in long, narrow, slender ribbons melting at 67.5°.

2. 1:1'-Dichloronaphthalene was prepared by Atterberg's method (*Ber.*, 1876, 1732) from β -dinitronaphthalene. The sulphonation product consists of a single acid, the chloride of which crystallises from petroleum spirit in minute aggregates melting at 114°; the amide crystallises from alcohol in tufts of small slender needles melting at 228°. The corresponding trichloronaphthalene crystallises from alcohol in very long slender needles melting at 131°.

3. 1:4'-Dichloronaphthalene yields two acids on sulphonation; of these, one is formed in small quantity only, and has not been completely examined. The chief product yields a chloride, which crystallises from benzene in aggregates of long, flat, thin, narrow plates melting at 139.5°; the amide crystallises in small prismatic aggregates melting at 204°. The corresponding trichloronaphthalene crystallises from alcohol in long slender needles melting at 103°. On hydrolysing the acid at 260–265° with concentrated muriatic acid, pure 1:4-dichloronaphthalene was obtained, which crystallises from alcohol in short flat thin scales melting at 106.5°.

αα-Dichloronaphthalenes.*ββ-Dichloronaphthalenes.**αβ-Dichloronaphthalenes.**αβ Dichloronaphthalenes.*

4. 1 : 2-Dichloronaphthalene is found to yield a mixture of an α- and a β-sulphonic acid, the former constituting about two-thirds of the product.

The chlorides of the two acids require to be mechanically separated after crystallisation from benzene.

α-Acid.—The chloride crystallises from benzene, in which it is very soluble, in large prismatic forms melting at 104°; the *amide* crystallises from alcohol in tufts of small slender needles, and melts at 217°. The corresponding *trichloronaphthalene* crystallises from alcohol in short flat needles melting at 78.5°. On hydrolysis with concentrated muriatic acid at 230°, the chloride gave pure 1 : 2-dichloronaphthalene melting at 35°.

β-Acid.—The chloride of the β-acid is less soluble in benzene, and crystallises in aggregates of small prisms melting at 167°; the *amide* crystallises from dilute alcohol in short slender white needles melting at 190°. The corresponding *trichloronaphthalene* crystallises from alcohol in slender needles and melts at 91°. On hydrolysis with concentrated muriatic acid at 260–265°, the β-chloride gave pure 1 : 2-dichloronaphthalene melting at 35°.

5. 1 : 3-Dichloronaphthalene.—On sulphonation this yields a mixture of an α- and a β-acid, the former constituting about four-fifths of the product.

The chloride of the α-acid crystallises from benzene in well-defined prisms melting at 148.5°, and crystallographically identical with those of the chloride of Widman's dichloronaphthalene-α-sulphonic acid; the *amide* is sparingly soluble in alcohol and crystallises in flocks of microscopic needles melting at 272°. The corresponding *trichloronaphthalene* crystallises from alcohol in long slender flat needles melting at 103°. On hydrolysis with concentrated muriatic acid at 230°, the α-chloride gave pure 1 : 3-dichloronaphthalene, which crystallised in long slender ribbons melting at 61°.

The β-acid, although the minor product of sulphonation, constitutes the sole product when the sulphonation product is heated in a dry atmosphere at 160° for eighteen

hours. Its *chloride* is very soluble in benzene and crystallises best from a mixture of benzene and petroleum spirit in long narrow four-sided prisms melting at 121° ; the *amide* crystallises from alcohol in tufts of short, very slender needles, and melts at 228° . The corresponding *trichloronaphthalene* is sparingly soluble in hot alcohol, and crystallises in short slender needles melting at 113° . On hydrolysis with concentrated muriatic acid at $260-265^{\circ}$, the β chloride gave pure 1:3-dichloronaphthalene melting at 61° .

6. 1:2'-*Dichloronaphthalene* yields an almost uniform product on sulphonation, the proportion of isomeric acid formed being very small. The *chloride* of the chief product crystallises from benzene in transparent, slender, flat needles which rapidly became opaque on exposure to the air, and then melt at 118° ; the *amide* is sparingly soluble in alcohol, and crystallises in narrow slender ribbons melting at 226° . The corresponding *trichloronaphthalene* crystallises from alcohol in slender flat needles which, on standing in the solvent, became opaque and melted at 66° . On hydrolysis with concentrated muriatic acid at 230° , the chloride gave pure 1:2'-dichloronaphthalene, which crystallises from alcohol in small crystalline aggregates melting at 62.5° . The synthetical 1:2'-dichloronaphthalene, prepared by Erdmann's method, was found to melt slightly higher, viz., at $63-63.5^{\circ}$.

7. 1:3'-*Dichloronaphthalene* yields a uniform product on sulphonation. The *chloride* of the acid crystallises from benzene in magnificent prisms and melts at 151° ; the *amide* crystallises from alcohol in long slender needles melting at 216° . The corresponding *trichloronaphthalene* crystallises from alcohol in slender flat needles which become opaque on standing in the solvent and melt at 66° . On hydrolysis with concentrated muriatic acid at 230° , the chloride gave pure 1:3'-dichloronaphthalene, which crystallised from alcohol in long slender ribbons melting at 48° .

$\beta\beta$ -Dichloronaphthalenes.

8. 2:3-*Dichloronaphthalene*. To prepare this modification a solution of 1:2:3-trichloronaphthalene in alcohol heated at $60-70^{\circ}$ is treated with one-and-a-half times the theoretical quantity of 2 per cent sodium amalgam during one hour; the 1-dichloronaphthalene is purified by fractional steam-distillation and fractional crystallisation from alcohol. It crystallises in the manner described by Leeds and Everhard and by Widman, in thin lustrous scales and melts at about 120° . On sulphonation it yields a product containing an α -acid and probably a β -acid, the former constituting the chief product. The α *chloride* crystallises from benzene in lustrous slender narrow ribbons melting at 142° ; the *amide* is sparingly soluble in alcohol and crystallises in aggregates of small slender needles melting at 268° . The corresponding *trichloronaphthalene* crystallises from alcohol in long and very slender needles, and melts at 109.5° . On hydrolysis with concentrated muriatic acid at 230° , the α -chloride was found to yield pure 2:3-dichloronaphthalene, which crystallised from alcohol in the characteristic thin scales melting at 119.5° .

Isomeric Acid.—The salts of this acid have not yet been obtained in quantity sufficient for analysis. The *chloride* is very soluble in benzene and crystallises in opaque hemispherical aggregates melting at 178° ; on hydrolysis with concentrated muriatic acid at $260-265^{\circ}$ it gave 2:3-dichloronaphthalene melting at 119.5° . There can be little doubt that this acid has the constitution $[Cl_2 : SO_3H = 2 : 3 : 2']$.

9. 2:2'-*Dichloronaphthalene* yields an almost uniform product on sulphonation, the proportion of isomeric acid formed being very small. The *chloride* of the chief product crystallises from benzene in well-formed elongated prisms, and melts at 163.5° ; the *amide* crystallises from dilute alcohol in tufts of long slender needles, and melts at 218° . The corresponding *trichloronaphthalene* crys-

tallises from alcohol in minute plates and melts at $90.5-91^{\circ}$. On hydrolysis with concentrated muriatic acid at $260-265^{\circ}$, the chloride gave pure 2:2'-dichloronaphthalene, which crystallised from alcohol in large thin laminæ melting at 114° .

10. 2:3'-*Dichloronaphthalene* affords an almost uniform sulphonation-product, the proportion of isomeric acid formed being small. The *chloride* of the chief product crystallises from benzene in radiate groups of long slender prismatic needles melting at 136° ; the *amide* is sparingly soluble in alcohol and crystallises in small aggregates of prismatic needles melting at 269° . The corresponding *trichloronaphthalene* is sparingly soluble in alcohol and crystallises in small slender needles melting at 113° . On hydrolysis with concentrated muriatic acid at 230° , the chloride gave pure 2:3'-dichloronaphthalene crystallising from alcohol in long narrow ribbons melting at 135° .

It is noteworthy that the chlorides of the β sulphonic acids require prolonged heating at a higher temperature than those of the α acids to effect their hydrolysis; and that on distillation with phosphorus pentachloride they give a smaller yield of trichloronaphthalene.

In the accompanying table the formulæ of the dichloronaphthalenes are given in first column, those of the acids into which they are converted on sulphonation are given in the second, and the third comprises the trichloronaphthalenes obtained from the dichloronaphthalene-sulphonic acids. The evidence on which the constitution of the tri-derivatives here given is based has been incidentally given in previous papers (*cf. Proc. Chem. Soc.*, 1889, 48; 1890, 11), and will be summarised in a forthcoming account of the trichloronaphthalenes.

(To be continued).

NOTICES OF BOOKS.

Gems and Precious Stones of North America. A Popular Description of their Occurrence, Value, History, Archæology, and of the Collections in which they Exist; also a Chapter on Pearls, and on Remarkable Gems Owned in the United States. Illustrated with Eight Coloured Plates and numerous Minor Engravings. By GEORGE FREDERIC KUNZ. New York: The Scientific Publishing Company.

THIS beautifully got up and richly illustrated volume is not easy to characterise. It is not a monograph of the precious stones of North America, including, as it does, much matter of which the mineralogist can take no account. Still, he will find here abundant valuable information on the North American localities in which such stones have hitherto been found. The author is of opinion that, e.g., the daily yield from the South African diamond mines would exceed in value the entire yearly out-put of precious stones in the United States. He gives an account of alleged valuable gems which when they came into qualified hands were found to be nearly worthless. An instance of this kind is the supposed "Blue Ridge Sapphire," which, after being paraded as the "Georgia marvel," and valued at 50,000 dollars, proved to be a water-worn piece of rolled blue bottle-glass. A stone weighing nine ozs., found in North Carolina, was thought to be a genuine emerald, containing, curiously enough, a number of small diamonds! This treasure, on examination, proved to be merely "a greenish quartz crystal filled with long hair-like crystals of green byssolite or actinolite on which were series of small liquid cavities that glistened in the sun and led to the enclosed diamond theory." A supposed ruby of six ozs. in weight was merely a garnet of poor quality.

The author gives some hints which may save prospectors from much disappointment, at least as far as diamonds

are concerned. He explains the error—one of the many delusions contained in the writings of Pliny—that a diamond will not break if struck with a hammer. It is suggested that good specimens may have been destroyed by this rough and fallacious test. As the simplest criterion, the finder is advised to try if a specimen will scratch corundum. If it does so, and if it is not scratched by a diamond, it may safely be assumed to be a diamond. This subject naturally leads to the much disputed question of the origin of diamonds. The rocks in various parts of the United States where diamonds have been occasionally found have been compared with those of Kimberley, which are much more recent formations. Itacolumite, like that of Brazil, has been found in North Carolina, but no diamonds have actually been discovered in this formation. It has been recently contended that the diamond is not of terrestrial, but of cosmic formation. This theory receives some confirmation from the facts that diamonds have occurred in meteorites. In 1884, Sir H. E. Roscoe, as here quoted, stated in a paper read before the Literary and Philosophical Society of Manchester, that on digesting some of the "blue" soft diamond earth of South Africa in ether he obtained a small quantity of an aromatic crystalline body.

A singular fraud in connection with diamonds was carried out in New Mexico and Arizona about twenty years ago. A company was started for collecting the diamonds, rubies, &c., which were there plentiful. An agent of the projectors had made extensive purchases of rough diamonds in Hatton Garden, and with these the selected locality was "salted." A diamond weighing 108 carats was said to have been found, and 80,000 carats of rubies; but the rubies were merely garnets, the 108-carat diamond was a piece of quartz, and the smaller stones were found to have the peculiarities of African and Brazilian diamonds. The promoters are said to have realised 750,000 dollars.

The United States are richer in the varieties of corundum than in diamonds, and some beautiful specimens are here represented in their natural colours.

Turquoise is very abundant in New Mexico, and appears to have been valued as an ornament by the aborigines. The American specimens, however, like the Egyptian, do not retain their full blue colour, like the genuine Persian stones, but turn to a green.

A singular phenomenon is shown in the plate opposite p. 138. A tree which has been fossilised forms a natural bridge over a dell 45 feet in width. Fully fifty feet of the tree rests on the rock on one side, so that the trunk is visible for 100 feet. It is found to belong to the genus *Aracaria*, of which the Norfolk Island pine (*A. excelsa*) is a living specimen.

We find here an extensive chapter on pearls, and on nacreous shells, which have, of course, no other connection with gems beyond their being prized as ornaments. There is a curious figure of a pearl having a nucleus of clay. It seems that a company was formed for pearl-fishing by means of a submarine boat. The project seems very feasible, but it was not successful, as the company soon ceased to exist.

The fugitive character of the beauty of the opal is fully noticed. Of all its varieties, the fire-opal is most readily injured by moisture or sudden atmospheric changes. Specimens "have been known to lose their brilliancy whilst in a jeweller's safe or in a collector's cabinet." They not only lose their colour but become filled with flaws and cracks. The Mexican and Central American opals are said to be more liable to such changes than the Hungarian specimens. Concerning the Queensland opals the author says nothing.

A large portion of the fourteenth and fifteenth chapters is devoted to anthropology—a science which in the United States is cultivated with surprising zeal. We find here representations of polished figures executed by the aborigines in obsidian knives and mirrors of the same material, a mirror of iron pyrites, a "banner-stone" of

ferruginous quartz, &c. The author remarks that many of the aboriginal stone objects found in North America are marvels of skill in chipping, drilling, grinding, and polishing," and adds that no modern lapidary "could make anything more graceful in form and general outline than are some of the quartz discoidal stones found" in North Carolina.

In the last chapter the author takes up the commercial and statistical phase of his subject. To define precious stones he finds difficult. "Strictly speaking," he says, "the only precious stones are the diamond, ruby, sapphire, and emerald, though the term is often extended to the opal, notwithstanding its lack of hardness, and to the pearl, which is not a mineral but an animal product."

The term "gem" is limited to minerals hard enough to scratch quartz, and by archaeologists it is applied only to engraved stones.

The work before us is unique in its plan, no less than in its accurate and splendid illustration, and will be welcomed by all lovers of precious stones.

The Journal of the Royal Agricultural Society of England. Third Series, Vol. i., Part 1. London: Murray.

THIS issue contains very much valuable matter, not all of which, however, can legitimately fall under our notice.

The "Disposal of Sewage in Small Towns and Villages," by Mr. Clare Sewell Read, contains some sensible and appropriate remarks, mixed with utterances showing that the sewage question is not the writer's forte.

For cottages he prefers the dry-closet system, but his confidence in the removal of all dangerous impurities from sewage by a passage through 20 feet of soil seems very overstrained. He admits that "the curse of most sewage farms is that they have to deal with the largest volume of sewage when they want it least." His commendation of osiers as the best crop for irrigation beds is quite justified by facts.

"The Evolution of the Horse," by Prof. W. H. Flower, is a most valuable addition to biological literature, but it cannot be brought within our purview.

Prof. E. Kinch contributes a paper on basic cinder, otherwise known as Thomas slag, and its uses in agriculture. It appears that the make of steel in this country by the Thomas-Gilchrist process was last year nearly half a million tons, and in the whole world over 2½ million tons. The yield of basic slag was 700,000 tons, containing on an average 36 per cent of the basic calcium phosphate. The caution is given to farmers who use this manure never to mix it with ammonium sulphate, as it causes an escape of ammonia. The slag is pronounced a good phosphatic manure, especially on heavy clays, peats, and soils deficient in lime. On calcareous soils it is less efficient.

Twenty-Fifth Annual Report of the Alumni Association of the Philadelphia College of Pharmacy, for the Years 1888—1889. Philadelphia.

WE find in this Report a selection of papers which, if not exclusively devoted to chemistry, are not without a profound interest. In one entitled "Life in an Almshouse" we find the sad remark: "If you want anything done, no matter how intricate—if you want talent of any description you can find it in the almshouse."

The "Liabilities of the Profession of Pharmacy" contains some of what has been called the most hateful of vices for the especial benefit of the "Alumni." The speaker draws a novel distinction between trades and professions. In the former the object is money, or perhaps fame; in the latter it is the welfare of man, the advancement of knowledge, or the attainment of an ideal.

Action of Lime upon Raffinose.—L. Lindot.—In comparison with calcium saccharate, raffinose is insoluble.

CORRESPONDENCE.

MEDICAL OFFICERS OF HEALTH AND
PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—A short time since the Town Council of one of the largest towns in Lancashire met for the purpose of selecting a gentleman to fill the joint position of Medical Officer of Health and Public Analyst. The advisability of keeping these two offices quite distinct has recently been suggested in the CHEMICAL NEWS—a suggestion with which I most cordially agree—as so few medical men are competent to perform a public analyst's duties satisfactorily.

In the *Proceedings of the Institute of Chemistry*, Part 2, 1890, p. 48, attention is called to the desirability of urging upon those who have at their disposal the appointment of analysts to various official positions that "membership of the Institute should be an indispensable qualification." This is a step in the right direction, and if the Council of the Institute could see their way to take even more decisive action upon this point it would be for the benefit of the entire chemical profession.—I am, &c.,

ROWLAND WILLIAMS.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
June 2, 1890.

CHEMICAL NOTICES FROM FOREIGN
SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 20, May 19, 1890.

The Isomeric States of Chromium Sesquibromide.—A. Recoura.—The author has previously shown that chromium sesquichloride differs from the other salts of chromium by the fact that it may assume two distinct isomeric states, but presenting this character in common, that the oxide precipitated from both their solutions by alkalis is the sesquichloride of the violet series. He obtained the green sesquibromide by mixing a saturated solution of chromic acid with a solution of hydrobromic acid at about 50 per cent, employing it in large excess. The solution, evaporated down with heat, gives, when cold, fine green needles, having the composition $\text{Cr}_2\text{Br}_3\cdot 12\text{H}_2\text{O}$. They are extremely soluble in water and very deliquescent. The dilute solution passes in about an hour from a splendid green to a bluish shade, and in twenty-four hours to a violet. This change is accompanied by the liberation of heat. The sesquioxide precipitated from the solutions, whatever their state, is always that of the violet salts of chromium.

The Existence of a Crystalline Hydrate of Ferric Oxichloride, and on its Transformation into a Dimorphous Variety of Goethite.—G. Rousseau.—The decomposition of dilute solutions of ferric chloride was first pointed out by Senarmont. The study of this phenomenon was resumed by Debray, who found that very dilute solutions of ferric chloride are split up at about 70° into hydrochloric acid, and colloidal sesquioxide precipitable by sodium chloride. At 100° Graham's oxide is gradually converted into the modification of ferric oxide discovered by Saint Gilles. If very concentrated solutions of ferric chloride are operated upon, crystals are obtained of the formula $\text{Fe}_2\text{Cl}_3\cdot 2\text{Fe}_2\text{O}_3\cdot 3\text{H}_2\text{O}$.

Certain New Double Chromates.—M. Lachaud and C. Lepierre.—The authors have obtained double chromates of lead and of the alkaline metals, *i.e.*, of potassium in a brick-red, a yellow, and an orange modification, of sodium in a yellow and an orange form. With lithium they were less successful. Their experiments with barium, strontium, and calcium chromates have not led to results of importance.

Crystallisation of Alumina and of other Oxides in Gaseous Hydrochloric Acid.—P. Hautefeuille and A. Perrey.—Alumina prepared by the limited decomposition of the oxalate, if exposed to the action of hydrochloric acid at a pressure of three atmospheres and at a temperature below incipient redness, is converted into corundum. Amorphous titanous acid crystallises in the form of anatase and zirconia in rhombic tables.

Bouquet of Wines and Brandies.—A. Rommier.—The author, referring to his communication made to the Academy June 24, 1889, finds that active ellipsoidal ferment, if introduced into grapes when crushed at temperatures below 21°–22° multiplies more rapidly than the spores of the ferments found on the skins of the grapes; the action of the latter is paralysed. If a small quantity of an ellipsoidal ferment is added to grapes at temperatures above 21°–22°, the ferment added develops along with the natural ferment and modifies the bouquet of the wine. M. Martinand has made an *experimentum crucis* which seems to confirm the author's theory. He divided the grapes of one and the same vine into five lots, and added to each a different ferment; to (1) that of a must of cherries in full fermentation; (2) of Beaujolais; (3) of Burgundy; (4) of Champagne; (5) of Bordeaux. All these wines presented distinct flavours.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 48.

This number contains no chemical matter.

Vol. v., No. 49.

Report by M. Le Chatelier on the Manganese-Steel of Mr. Hadfield.—The Committee consider manganese steel well adapted for agricultural machinery, wagon wheels, horse shoes, the axles of rotation of a great number of machines, and in general for articles exposed to wear by friction or to fracture by shocks.

Report given in by H. Le Chatelier on behalf of the Committee of Chemical Arts on M. Henry's Slag Cement.—This cement is obtained by mixing blast-furnace slags of suitable composition previously soaked in water and finely ground with a certain proportion of slaked lime. The new product cannot be placed in the same rank as Portland cements of good quality, but its cost is less by at least one-half.

Vol. v., No. 50.

This number contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 6.

The Blue Flame of Common Salt, and the Spectroscopic Reaction of Copper Chloride.—G. Salet.—The well-known blue flame produced when salt is thrown upon a coke fire is due to traces of copper present in the fuel. The spectrum of the flame shows the bands of copper chloride.

Remarks on Formic Fermentation.—M. Berthelot.—The author has studied this phenomenon in the case of dung. He finds that the total heat given off is greater than that liberated in alcoholic fermentation.

Combustion- and Formation-Heats of Urea.—MM. Berthelot and Petit.—A thermo-chemical paper not adapted for abridgment.

Heat Developed by the Action of Oxygen upon the Blood.—M. Berthelot.—The absorption of oxygen tends to raise the temperature of the blood in the lungs, whilst the production of carbonic acid and of watery vapour tends to lower it.

On the different States of the Graphite Carbons, and on the Corresponding Chemical Derivatives.—M. Berthelot and P. Petit.—The authors have analysed and studied the graphite of cast-iron, pyrographitic oxide, amorphous graphite, and electric graphite.

Combustion- and Formation-Heat of the Graphitic and Pyrographitic Oxides.—M. Berthelot and P. Petit.—A thermo-chemical supplement to the foregoing memoir.

No. 7.

A Bichloric-propionic Aldehyd.—W. Spring and E. Tait.—By the direct action of chlorine, propylic alcohol only yields one bichloro-derivative of propionic aldehyd, accompanied by secondary products. The introduction of a third atom of chlorine into the molecule demands special consideration.

Thermo-chemical Researches on Silk.—Leo Vignon.—The author has undertaken to ascertain if the absorbent power of silk, raw or ungummed, in presence of different reagents, gives rise to phenomena which may be measured thermically.

The Use of Tannins to Prevent Crock in Steam Boilers.—Leo Vignon.—Free tannins attack the boiler plates. Tannins associated with an excess of sodium carbonate present the same inconvenience. The influence of sodium carbonate is sensibly nil, and it is to be recommended.

Detection of Benzoic Acid in Alimentary Substances.—E. Mohlor.—This process will be given at some length.

Certain Derivatives of Erythrite.—E. Grimeaux and Ch. Cloes.—An account of hydrofurfuran, and the bromhydrines of erythrite.

On the Dispersion of Watery Solutions.—M. Barbier and L. Roux.—This memoir cannot be usefully reproduced without the accompanying diagrams and tables.

Remark on the Specific Dispersive Power of Aqueous Solutions.—MM. Barbier and Roux.—The specific dispersive power for a given substance varies very slowly with the concentration. This variation is, according to the cases, sometimes increasing and sometimes decreasing, but always very slight. Its mean value is common to all the substances examined.

Justus Liebig's Annalen der Chemie.
Vol. ccliv., Part 1.

The Alkylloxalic Acids, the Dichlorglycolic Ethers, the Alkylloxalic Chlorides, and the Tetra-alkyl or Semiorthoxalic Ethers.—R. Anschütz.—Not susceptible of useful abridgment.

Formulae for Calculating the Molecular Volumes of Organic Compounds.—W. Lossen.—This memoir does not admit of abridgment.

Communications from the Chemical Institute of the University of Geneva.—These comprise memoirs by S. Levy and F. C. Witte on symmetric tetrachloro-diethyl, and by S. Levy and A. Curchod on symmetric tetrachloroacetone.

Communication from the Organic Laboratory of the Royal Technical High School at Aachen.—This includes a second treatise by A. Michaelis on syntheses effected by means of sodiumphenylhydrazine, and a memoir by O. Burchard on ethylenphenylhydrazine.

MEETINGS FOR THE WEEK.

TUESDAY, 10th.—Royal Institution, 3. "The Natural History of Society," by Andrew Lang.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 11th.—Microscopical, 8.
THURSDAY, 12th.—Royal Institution, 3. "Flame and Explosives," by Prof. Dewar, M.A., F.R.S.
— Royal, 4.30.
— Mathematical, 8.
— Society of Arts, 8. "The Rationale of Indian Railways," by Sir Theodore C. Hope.
FRIDAY, 13th.—Royal Institution 9. "The Physical Foundation of Music," by Prof. Silvanus P. Thompson.
— Astronomical, 8.
— Quekett Club, 8.
SATURDAY, 14th.—Royal Institution, 3. "The Ballad Music of the West of England" (with musical illustrations), by Rev. S. Baring-Gould, M.A.

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THE PATENTEE'S MANUAL.

By JAMES JOHNSON,
Middle Temple, Barrister-at-Law, and

J. HENRY JOHNSON,
Assoc. Inst. C.E., Solicitor and Patent Agent.

This work explains clearly and concisely the Law and Practice of Letters Patent for Inventions, with references to all reported cases. The Appendix contains the Patent Statutes, Patent Office Rules, Forms, and Fees, the Rules of the Law Officers and of the Privy Council, the International Convention, and particulars of the Patent Laws of all Foreign States and British Possessions. The copious Index forms a clear analysis of the whole.

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BRITISH ASSOCIATION FOR THE
ADVANCEMENT OF SCIENCE, 22, Albemarle Street,
London. W.

The NEXT ANNUAL GENERAL MEETING will be held at LEEDS, commencing on Wednesday, September 3.

President Elect—
Sir FREDERICK AUGUSTUS ABEL, C.B., D.C.L., D.Sc.,
F.R.S., V.P.C.S.

NOTICE to CONTRIBUTORS of MEMOIRS.—Authors are reminded that, under an arrangement dating from 1871, the acceptance of Memoirs and the days on which they are to be read are now as far as possible determined by Organising Committees for the several Sections before the beginning of the Meeting. It has, therefore, become necessary, in order to give an opportunity to the Committees of doing justice to the several Communications, that each Author should prepare an Abstract of his memoir of a length suitable for insertion in the published Transactions of the Association, and the Council request that he will send it, together with the original Memoir, by book-post on or before August 6, addressed thus:—"General Secretaries, British Association, 22, Albemarle Street, London, W. For Section —." Authors who comply with this request, and whose papers are accepted will be furnished before the Meeting with printed copies of their Reports or Abstracts. If it should be inconvenient to the Author that his paper should be read on any particular day, he is requested to send information thereof to the Secretaries in a separate note.

LIFE MEMBERSHIP German Chemical Society; Journals from January, 1879, to date. Bound half-calf, 1879 to 1884, inclusive; remainder in numbers, offer at once. Cheap, immediate disposal. Member 33 years old.—Address, "Books," W. Porteous and Co., Glasgow.

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FOR SALE.—Analytical Balance, in good condition, by Becker and Sons, Rotterdam. Charge up to 50 grammes in each pan, with rider apparatus; French polished, in glass case.—Apply, Mrs. Graham, 5, Dartmouth Terrace, Lewisham, S.E.

THE CHEMICAL NEWS.

VOL. LXI. No. 1594.

A NEW AND EFFICIENT APPLIANCE FOR THE DETECTION OF HYDROCARBONS AND OTHER COMBUSTIBLE GASES WHEN IN ADMIXTURE WITH THE ATMOSPHERE.

By H. N. WARREN, Research Analyst.

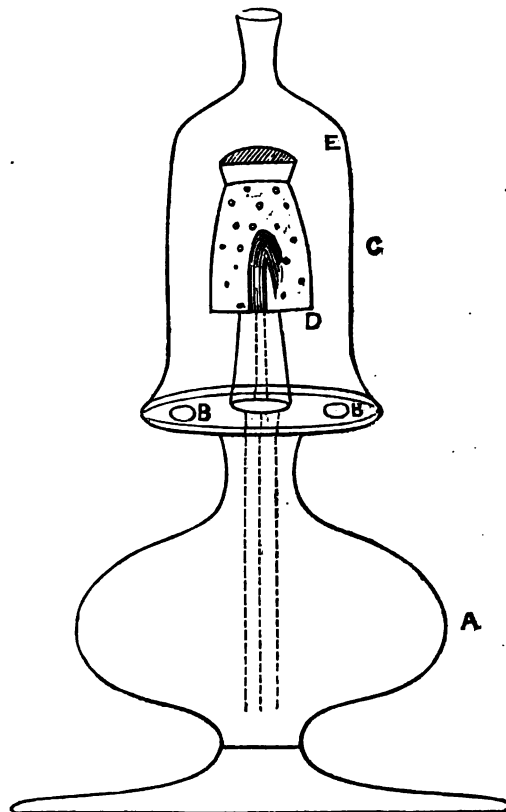
THIS peculiar form of gas-testing apparatus was introduced by the author at the commencement of the year, and is intended chiefly for the detection of suspected escapes of coal-gas when in confined spaces, such, for instance, as private houses, laboratories, &c.

Experiments with a view of studying more closely the condensing action of platinum when in various forms of division were the chief motor which led to the construction of the same. Thus, if asbestos (for convenience sake in the form of yarn) be introduced into a solution of platonic chloride, and, after drying, ignited in a closed crucible, the substance, as is well known, has conferred upon it the property of condensing gases upon its surface, due to the impregnation of what is known as platinum black. This method of rendering asbestos sensitive is, however, attended with several inconveniences, both on account of the disengagement of acid during ignition, thus rendering the texture rotten, and at the same time retarding surface-action by the formation of magnesium salts. To obviate these difficulties the writer has substituted with advantage for the chloride that of platonic oxalate, and by so doing has obtained a modified action of peculiar sensitiveness. This compound is readily procured by saturating asbestos yarn of finest quality with a strong solution of platonic oxalate, obtained by dissolving the hydrate of that metal in oxalic acid and, after drying, igniting the same in a porcelain crucible. If a sample of so-prepared asbestos be now introduced into a mixture of hydrogen and oxygen gases combination at once takes place, accompanied by the usual phenomenon; but if the said mixture be now substituted by one of coal-gas replacing the hydrogen, no action is the result. Withdraw now the sensitive wick and heat to 80° F. and replace the same in the mixture, quite a different result is at once obtained, the wick being quickly raised to incandescence, and continues as long as the slightest mixture of gas remains; so sensitive, in fact, is the reaction that 0.5 per cent by volume of coal-gas or other hydrocarbons, when in admixture with the atmosphere, is at once readily detected.

The subjoined figure, representing a section of the apparatus when in use, will perhaps serve to more clearly demonstrate the same, A serving as the basis or reservoir of the lamp, and containing petroleum spirit, which is employed as a fuel for the same, and surmounted by a gallery running round the upper part and pierced with two apertures at B B, intended to collect the air desired when applying the chimney, C. In using the apparatus the wick, consisting of platinised asbestos, is first inserted in its holder and a light applied to the same. The flame caused by the combustion of the petroleum spirit may be now conveniently extinguished, leaving the uppermost part of the wick red-hot, which continues to glow while any petroleum spirit remains in the reservoir. While the wick is still glowing there is placed over it the copper thimble, D, which is perforated with numerous small holes, and containing a further coil of platinised asbestos, &c., in close proximity.

The reaction may thus be readily explained:—The heated asbestos, fed by the petroleum spirit, naturally produces sufficient heat to maintain the secondary coil at

to a temperature required for producing effects when in contact with hydrocarbons. If the so-prepared lamp be now introduced into a room where an explosive atmosphere is prevalent, the glass chimney at once samples



the atmosphere by causing an upward draught, the which, passing over the heated coil immediately raises the same to incandescence.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

A METHOD FOR THE DETERMINATION OF IODINE IN HALOID SALTS.*

By F. A. GOOCH and P. E. BROWNING.

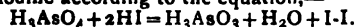
Few problems of analysis have been more discussed than the estimation of iodine accompanying chlorine and bromine in haloid salts; and yet the constant succession of new processes is sufficiently indicative that the solution of the question is not generally regarded as satisfactorily settled. The method of Fresenius, according to which iodine is liberated by nitrous acid, collected in carbon disulphide, and titrated by sodium thiosulphate, finds ready acceptance for the determination of small amounts of iodine; but when the quantity of iodine to be estimated is considerable, the method is unwieldy. Probably the process most generally in use is that based upon the liberation of iodine by means of a ferric salt, and the titration of the distillate by one or other of the well-known iodometric methods. The latter method is fairly

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., March, 1890.

accurate, but the requirement of special apparatus for properly condensing the distillate is detrimental to rapidity and ease of execution. In this process the amount of iodine set free should be measured exactly by the reduction of the ferric salt, and were the ferrous salt produced in the course of the action sufficiently stable, the determination of its amount might be substituted for the titration of the iodine, and so the collection and further treatment of the distillate might be dispensed with; but ferrous salts are too sensitive to atmospheric influence to preserve under the conditions of this process their own degree of oxidation, and the amount of iron found in the ferrous condition cannot be made to serve as a trustworthy indication of the reducing action which actually takes place in the separation of the iodine. The advantage of replacing the collection and examination of the distillate by treatment of the residue is, however, so great as to constrain us to search for some substitute for the ferric salt, which, by virtue of easy reducibility, may act as a liberator of iodine from hydriodic acid, and, at the same time, by reason of stability after reduction, shall register accurately the quantity of iodine set free in the reducing process. The results of our experience are contained in the following account:—

Strong sulphuric acid, as is well known, acts upon an iodide in a way to liberate iodine at the cost of its own loss of oxygen, though by simple dilution of the mixture thus formed the action is reversed, the iodine going back into the form of hydriodic acid, and the products of the reduction of sulphuric acid again taking back their oxygen and re-forming the acid. In the presence of any substance easily reducible by the deoxidation products of sulphuric acid the liberation of iodine, by the action of that acid upon iodides, should take place without interference, and even more easily and completely than in the absence of such a substance, while the sulphuric acid should remain at the end of the process in its original form. If the products of reduction which appear in such a case in the place of those of the sulphuric acid should be neither readily oxidisable nor easily volatilisable, it ought to be possible to remove by heat the iodine set free in the action without disturbing the record kept of its amount by the reduced substance remaining in the residue.

The qualities of arsenic acid suggest it as a substance likely to possess just these qualities; for, though arsenious acid is converted into arsenic acid by the action of iodine in alkaline solution, in acid solution the reverse is true to at least a limited extent, and arsenic acid liberates iodine according to the equation,—



In company with sulphuric acid of such strength as to liberate the iodine from hydriodic acid, the reduction should fall in the end upon the arsenic, and the arsenious oxide produced should, under proper conditions, preserve the record of the iodine liberated and removed by volatilisation. We therefore undertook experimentation upon this line, and the accompanying table shows the results of a preliminary investigation of the mode of action of a mixture of sulphuric and arsenic acids upon an alkaline iodide. In making these tests a standard solution of potassium iodide was put into a test-tube, a solution of potassium arseniate was added, sulphuric acid mixed with its own volume of water was introduced, the volume of the liquid was adjusted, a film of kerosene 3 m.m. thick was placed upon the surface of the liquid, and the whole was gently heated and agitated. Kerosene was chosen in preference to other solvents of iodine on account of its lightness, which makes it float upon the mixture, and its high boiling-point, which permits the application of heat to hasten and complete the reaction. Its disadvantage is the persistency with which it adheres to the walls of the test-tube, so that washing with alcohol (or other solvent) after the completion of each test is necessary to prevent the transfer of the iodine of one test to the test next succeeding. The data of these experiments are indicated in the headings.

It will be noted that in Series A, in which the absolute amount of iodine employed, its proportion to the entire volume, and the amount of the arsenic salt remained the same, the proportion of sulphuric acid being the variable element, it is shown that the proportion of sulphuric acid should reach at least twelve parts by volume in one hundred of the solution in order that the maximum distinctness of the test may be developed. An excess of sulphuric acid beyond this proportion is not disadvantageous.

In Series B the proportion and absolute amount of iodine vary as well as the proportion of acid, while the quantity of arsenic remains invariable. The results of this series confirm those of the previous series as to the proper proportion of sulphuric acid to be used, and the sensitiveness of the test is shown to reach (in round numbers) one part by weight of iodine in six hundred thousand parts of the solution.

The tests of Series C indicate plainly that it is the sulphuric acid which is the potent agent in liberating the iodine, the experiment in which acetic acid was substituted for sulphuric acid being particularly noteworthy in this connection. The presence of arsenic acid increases the sensitiveness of the reaction, but its addition beyond a very moderate amount does not appear to be necessary or advantageous. The presence of a chloride or bromide does not impair the delicacy of the test.

The quantities of iodine taken in the experiments just described were necessarily small, and the question arises naturally as to whether the course of action would be similar in the presence of larger amounts of that substance and the correspondingly greater amount of arsenious oxide which is produced with its tendency to reverse the reaction according to which the elimination of iodine proceeds. The solution of this question was reached in the following experiments:—

To 50 c.m.³ of liquid containing 10 c.m.³ of sulphuric acid [1 : 1], and 1 c.m.³ of a decinormal solution of iodine in potassium iodide (0.001265 gm. of the former in 0.0018 gm. of the latter) was added 1 c.m.³ of a decinormal solution of arsenious oxide (0.00495 gm.), an amount ten times as much as would be necessary to convert the iodine into hydriodic acid were the solution alkaline. The colour of the iodine vanished gradually under the action of the arsenious acid, but was restored by the addition of 1 gm. of hydrogen potassium arseniate, and again dispelled by another portion of arsenious acid equal in amount to that introduced at first. Heat was applied at this point with the result that the colour of the iodine showed again faintly, and upon boiling the liquid until its volume decreased to 25 c.m.³ it became colourless and yielded no iodine when agitated with nitrous acid and chloroform.

An experiment differing from the last in that thirty times as much arsenious oxide and iodine were taken, gave similar results.

It is plain, therefore, that the arsenious acid and arsenic acid exert opposite effects under the conditions of these experiments, and that one or the other prevails according to the proportionate composition of the solution, the degree of dilution, and the temperature.

The experiments detailed in the following statement were intended to determine the conditions best adapted to eliminate the iodine from such quantities of potassium iodide as would ordinarily be dealt with in the course of analysis.

A solution of potassium iodide was placed in an Erlenmeyer beaker of 300 c.m.³ capacity, followed by a solution of potassium arseniate and by dilute sulphuric acid [1 : 1], and the volume of the liquid was diluted to about 100 c.m.³. A mark was put upon the beaker to indicate the level to which the liquid was to be reduced, a spiral of platinum wire was placed in the solution to prevent explosive ebullition, and the contents of the flask were boiled until the desired degree of condensation was reached. Colourlessness of the liquid at this point,

Series A.								
KI.	Grms. of iodine to c.m.* of solution.	H ₂ KAsO ₄ .	H ₂ SO ₄ .	H ₂ SO ₄ (strong) in 100 parts by volume	NaCl.	KBr.	Total vol. c.m.*	Reaction or iodine.
Grm.		Grm.	[1:1]. c.m.*		Grm.	Grm.		
0'0001	I : 132000	I	2	10 : 100	—	—	10	Faint.
0'0001	I : 132000	I	2	10 : 100	—	—	10	Faint.
0'0001	I : 132000	I	2'5	12'5 : 100	—	—	10	Faint.
0'0001	I : 132000	I	2'5	12'5 : 100	—	—	10	Distinct.
0'0001	I : 132000	I	3	15 : 100	—	—	10	Distinct.
0'0001	I : 132000	I	4	20 : 100	—	—	10	Distinct.
0'0001	I : 132000	I	4'5	22'5 : 100	—	—	10	Distinct.
0'0001	I : 132000	I	5	25 : 100	—	I	10	Distinct.
Series B.								
0'0005	I : 26400	I	2'5	12'5 : 100	—	—	10	Distinct.
0'000133	I : 99000	I	2'5	12'5 : 100	—	—	10	Distinct.
0'0001	I : 198000	I	3	10 : 100	0'007	—	15	Faint.
0'000067	I : 198000	I	2'5	12'5 : 100	—	—	10	Faint.
0'000067	I : 198000	I	2'5	12'5 : 100	—	I	10	Faint.
0'0001	I : 198000	I	5	16'6 : 100	0'005	—	15	Distinct.
0'0001	I : 198000	I	5	16'6 : 100	0'005	—	15	Distinct.
0'0001	I : 264000	I	2'5	6'25 : 100	—	—	20	Invisible.
0'0001	I : 264000	I	2'5	6'25 : 100	—	—	20	Faint.
0'0001	I : 264000	I	5	12'5 : 100	—	—	20	Faint.
0'000033	I : 396000	I	2'5	12'5 : 100	—	—	10	Faint.
0'000033	I : 396000	I	2'5	12'5 : 100	—	—	10	Faint.
0'000033	I : 594000	I	5	16'6 : 100	0'005	—	15	Faint.
Series C.								
0'0020	I : 8000	I	None. Acetic acid 1'5 grm. (absolute).		—	—	12	Invisible.
0'0010	I : 13200	—	5	25 : 100	—	—	10	Distinct.
0'0002	I : 66000	—	5	25 : 100	—	—	10	Faint.
0'0010	I : 13200	0'2	5	25 : 100	—	—	10	Marked.
0'0001	I : 132000	0'2	5	25 : 100	—	—	10	Distinct.
0'000033	I : 198000	0'5	1'25	12'5 : 100	—	—	5	Faint.
0'000033	I : 198000	0'5	1'25	12'5 : 100	—	—	5	Faint.
0'0001	I : 264000	2'0	4	10 : 100	—	—	20	Faint.
0'0001	I : 264000	2'0	6	15 : 100	—	—	20	Faint.

though a fair indication of the absence of free iodine, is no indication that the hydriodic acid has been completely decomposed, and so, in the event of finding the liquid colourless, it was first cooled and shaken with chloroform to prove or disprove the absence of free iodine, and then tested for the presence of hydriodic acid by shaking with nitrous acid and chloroform.

An inspection of these results shows at once that when the larger amounts of iodine are to be eliminated the proportion of sulphuric acid to the final volume after boiling needs to be increased somewhat beyond that which is necessary to set free very small portions, such as were dealt with in the experiments of the earlier series.

(To be continued).

SOME POINTS IN THE DETERMINATION OF SILICA IN SILICATES BY FUSION WITH ALKALINE CARBONATES.*

By JAMES P. GILBERT, S.B.

(Concluded from p. 272).

THE fourth point considered was the possibility of obtaining the silica in a purer state, that is to say, to decrease the amount of the residue left after treatment with hydrofluoric acid. This residue may be due to imperfect washing, or to the fact that alumina has been rendered insoluble

in hydrochloric acid by prolonged heating to a high temperature. The higher residues obtained in the cases in which the silica was heated to 280° C. point to the latter possibility. But it is not improbable, as will be mentioned later on, that under certain conditions the silica may enclose alkaline salts so that it is impossible to remove them completely by washing.*

In an interesting article by Lindo,† on the analysis of glass, I met the recommendation that the watery solution of the fusion be diluted to a very large bulk, so that on acidifying with hydrochloric acid there shall be no precipitation of silica. In this way he obtained, on evaporation, what he called "vitreous silica," in distinction from the ordinary "amorphous silica." This vitreous silica, he says, is so easily washed that time is gained in the analyses to compensate for that lost in the evaporation of the solution. Lindo takes it for granted that one cannot get all the silica by the ordinary process of dehydration, and that the last traces of it cannot be got out of the filtrate unless there is sufficient iron oxide or alumina present to effect its complete precipitation. In the analysis of glass, he added a known amount of ferric chloride to the filtrate from the alumina, and by precipitating this iron with ammonia the last traces were obtained.

The following analyses of glass were made according to his directions. The powdered glass, about 1 grm., was

* In this connection it is interesting to note that all the residues left on treatment with hydrofluoric acid, in the two slags analysed, contained manganese, which may point to an insoluble compound of manganese with the alkaline salts.

† CHEMICAL NEWS, vol. ix., No. 1546.

fused with 5 grms. of sodium and potassium carbonates, and the mass treated with about 400 c.c. of boiling water until it was thoroughly disintegrated. On acidifying with hydrochloric acid, a clear solution was obtained. This was evaporated to dryness on a water-bath, heated to 125° C., and, as recommended by Lindo, the silica thus obtained again fused and treated as before. This silica obtained from the second fusion was weighed, and then treated with hydrofluoric acid. The two filtrates were combined and evaporated to dryness, heated to 125° C. for one hour, and the residue, insoluble in hydrochloric acid and water, filtered off; this is given in the third column. The first three analyses are of German "half-white" glass; the last two, of Bohemian white glass.

TABLE IV.—*Determinations of Silica in Glass. (Lindo's Method).*

	I. Silica obtained after two fusions. Per cent.	II. Residue from Column I. with hydro- fluoric acid. Grm.	III. Silica ob- tained from the filtrates. Grm.	IV. Total silica. Per cent.
1.	73.03	0.0003	0.0058	73.58
2.	71.81	0.0008	0.0125	73.06
3.	72.50	0.0004	0.0084	73.22
4.	71.96	0.0000	0.0051	71.43
5.	71.25	0.0007	0.0060	71.70

In this case it is seen that a considerable portion of the silica fails to be dehydrated by one evaporation and heating to 125° C. The silica obtained in this way is very compact, and the washing, as claimed by Lindo, is very easily done. The purity of the silica thus obtained (shown by the small residue left on treatment with hydrofluoric acid) is doubtless in part due to the facility with which the silica is washed; for it is conceivable that, when the silica is separated from a concentrated solution of alkaline salts, it may enclose particles of the liquid which may not be easily washed out. But this high purity, as compared with the silica obtained from the slags and the felspar, may be due to the absence of any large amount of alumina in the glass.

To see what would be the character of the silica obtained from the first slag by large dilution of the solution of the fused mass before acidifying, the following determinations were made:—

TABLE V.—*Amount of Foreign Matter in Silica obtained from Lime Slag. (Lindo's Method).*

	I. Weight of silica obtained from slag. Grm.	II. Residue from Column I. with hydrofluoric acid. Grm.	
1.	0.2755	0.0008	Silica obtained by evaporation to dry- ness on water-bath.
2.	0.2610	0.0010	
3.	0.2871	0.0008	Silica obtained by evaporation to dry- ness and heating to 125° C.
4.	0.2683	0.0012	
5.	0.2506	0.0036	Silica obtained by evaporation to dry- ness and heating to 280° C.
6.	0.3113	0.0043	

These figures would seem to justify the inference that in the presence of considerable alumina it is not possible, even by large dilution, to get as pure silica as is easily obtained when only salts of the alkalis or alkaline earths are present.

The foregoing determinations confirm the statement that the ordinary process of fusion with alkaline carbonates and evaporation to dryness cannot always be relied on to render all the silica insoluble. No experiments were made to determine the effect of repeated evaporations to dryness with hydrochloric acid.

When the evaporation is carried out in the presence of free sulphuric acid the results are more satisfactory, but, as Craig says, the amount of alkaline sulphates introduced seriously interferes with the determination of the bases present.

A comparison of results obtained from a sample of quartz by evaporation with hydrochloric and sulphuric acids is given below.

Silica by evaporation to dryness with hydrochloric acid and heating to 120°. Per cent.	Silica by evaporation to dryness with sulphuric acid. Per cent.
98.95	99.43
98.60	99.67
98.79	99.51
	99.70

In these determinations I followed Lindo's recommendation of diluting largely before acidifying, and the residue left, on treatment with hydrofluoric acid, was very small. The first two determinations by sulphuric acid were done by decomposing the dilute watery solution of the fusion with hydrochloric acid, evaporating to dryness, and then adding strong sulphuric acid in excess and heating on an iron plate until copious fumes of sulphuric acid were given off for several minutes. The silica was in appearance the same as obtained by Lindo's method with the aid of hydrochloric acid only. But in the last two the watery solution of the fusion was decomposed directly by sulphuric acid in considerable excess, and then evaporated as before. The silica obtained in this way was very bulky and gelatinous.

These results seem to justify the recommendation that has been made; namely, that in the analysis of silicates the silica is best determined by dehydration with sulphuric acid (in cases where it is not inadmissible by the presence of lime, barium, lead, &c.), and that the bases should be determined, after the decomposition of the silicate, by hydrofluoric acid.

THE ELECTROLYSIS OF METALLIC PHOSPHATES IN ACID SOLUTION.*

By EDGAR F. SMITH.

SOME experiments on the action of the current upon metallic phosphates have been published by Moore,† and more recently Brand‡ has communicated his experience with the pyrophosphates dissolved in an excess of sodium pyrophosphate and also in ammonium hydroxide or carbonate. The experiments in this paper relate wholly to the deposition of metals from the solutions of their phosphates in normal phosphoric acid. The course pursued in the preparation of the solutions for electrolysis was to first precipitate the metals with an excess of disodium phosphate, dissolving the compound obtained in a measured volume of free phosphoric acid (sp. gr. 1.347), and then exposing this liquid to the action of currents of known strength. When operating upon mercuric solutions, prepared in the manner indicated, the deposition of the metal in the early part of the experiment was perfectly satisfactory, but as the decomposition advanced, a heavy white precipitate appeared in the solution, and, although it gradually suffered reduction, the metal that separated was so fluid-like that it mechanically carried down impurities, hence was unfit for electrolytic determinations, and the experiments in this direction were consequently suspended. Mercurous phosphate proved to be insoluble, or nearly so, in phosphoric acid. This is also the case with bismuth and lead phosphates, therefore neither of these metals was available in the proposed experiments.

* *American Chemical Journal*, xxii., No. 3.

† *Chem. News*, liii., 209.

‡ *Zeit. für Anal. Chem.*, xxviii., 581.

Copper.

To a solution containing 0.0996 grm. metallic copper, as sulphate, 10 c.c. Na_2HPO_4 (sp. gr. 1.0358) and $\frac{3}{4}$ c.c. H_3PO_4 (sp. gr. 1.347) were added. The precipitated copper phosphate, dissolved in $\frac{1}{2}$ c.c. of acid, so that the deposition of metal occurred in the presence of 3 c.c. of free phosphoric acid. The total dilution with water amounted to 125 c.c. The current employed gave 0.15 c.c. oxyhydrogen gas per minute. The copper deposit weighed 0.0997 grm. The metal precipitation was allowed to continue through the night. Later, two additional experiments were arranged in every respect similar to the one just described, increasing the current, however, to 0.5 c.c. oxyhydrogen gas per minute. The copper found was in (a) 0.0990 grm., and in (b) 0.0994 grm. The addition of an excess of ammonium hydroxide to the filtrates did not produce the slightest blue colouration. The metallic copper from the above experiments showed a rich red colour. The metallic lustre observed upon the metal deposited from solutions containing other free acids, e.g., HNO_3 , was not noticed here. That the conditions of the preceding depositions will answer for the separation of copper from other metals is evident from the results recorded below. Strong currents deposit metallic iron and other metals from their phosphates in phosphoric acid solution, while they are unaffected by the feeble currents.

Copper from Iron.

A solution containing 0.0996 grm. metallic copper, 0.1700 grm. metallic iron, 30 c.c. Na_2HPO_4 (sp. gr. 1.0358), and $\frac{3}{4}$ c.c. H_3PO_4 (sp. gr. 1.347) were diluted to 125 c.c. with water and exposed to the action of a current generating 0.6 c.c. oxyhydrogen gas per minute. The deposited copper weighed 0.0996 grm. Additional experiments verified this result. The filtrates contained no copper.

Copper from Aluminium.

Here the quantity of copper was the same as before, while the aluminium metal was 0.1000 grm., 20 c.c. Na_2HPO_4 (sp. gr. 1.0358) with 3 c.c. H_3PO_4 (sp. gr. 1.347). The total dilution was 100 c.c. The current gave 0.3 c.c. oxyhydrogen gas per minute. The copper deposited weighed 0.0995 grm.

Copper from Chromium.

Both metals were added as sulphates, the quantity of metallic chromium being in excess of that of the copper. The volume of alkaline phosphate was 20 c.c., and that of the phosphoric acid 3 c.c. The final dilution and current strength were the same as in the separation of copper from aluminium. The deposition was made during the night. The metal obtained equalled 0.0994 grm. It was brilliant red in colour, similar to that noticed frequently by chemists in the separation of these two metals from each other. The chromium was oxidised to chromic acid. The filtrate gave no indication of unprecipitated copper. A duplicate experiment afforded a similar result.

Copper from Zinc.

In this separation there were present 0.1500 grm. metallic zinc and alkaline phosphate and free phosphoric acid in the same quantities as with aluminium and chromium. The dilution was 100 c.c., while the current gave but 0.15 c.c. oxyhydrogen gas per minute. The deposited copper weighed 0.0993 grm. The filtrate gave no colouration upon the addition of an excess of ammonium hydroxide.

Copper from Cobalt.

With 0.0968 grm. cobalt and conditions similar to those just given under copper and zinc, except that the current had increased to 0.22 c.c. oxyhydrogen gas per minute, the deposited metal was found to be 0.0995 grm.

Copper from Nickel.

The nickel (0.1105 grm.) was present as chloride, while the conditions of experiment were similar to those in the preceding example. The deposit of copper weighed 0.0996 grm.

In all of the experiments given above the copper deposited rapidly from the cold solutions. Before interrupting the current the acid liquid was syphoned off and replaced by water. The deposits were washed with cold and hot water. Alcohol and ether were not used. The drying was done upon a warm iron plate. The current employed was obtained from ten ordinary "crowfoot" cells. In each experiment the poles of the battery were about $\frac{1}{2}$ inch apart.

Cadmium.

As this metal deposits from solutions containing free sulphuric acid,* it was expected that the same would occur in the presence of free phosphoric acid. This is proved by the following experiments:—10 c.c. cadmium sulphate (=0.1827 grm. Cd) were precipitated by an excess of Na_2HPO_4 (sp. gr. 1.0358) and the phosphate dissolved in 14 c.c. H_3PO_4 (sp. gr. 1.347). Total dilution, 100 c.c. The current gave 0.6 c.c. oxyhydrogen gas per minute. Two determinations were made in this way. The found metal was in (a) 0.1839 grm., and in (b) 0.1820 grm. The (a) deposit showed a little sponginess, and this doubtless caused it to give a higher result than required by the theory. The filtrates from these deposits gave no cadmium reactions upon applying the usual tests for that metal. In two other determinations, where the only change made in the conditions of experiment was the reduction of the current to 0.40 c.c. gas per minute, the deposited cadmium weighed in (a) 0.1828 grm. and in (b) 0.1833. These figures indicate complete deposition, and that the method is reliable. Cadmium does not, however, deposit as rapidly as copper under like circumstances. It was also found advisable towards the close of the experiment to increase the current strength. The acid liquid should always be removed from the dish in which the deposition occurs before the current is finally interrupted. The deposits were washed and dried as described with copper.

Cadmium from Zinc.

0.1827 grm. cadmium and 0.1500 grm. zinc (both as sulphates) were precipitated by 40 c.c. disodium phosphate, dissolved in 3 c.c. H_3PO_4 (sp. gr. 1.347) and added upon in the cold for twelve hours with a current giving 0.35 c.c. oxyhydrogen gas per minute. The cadmium deposit weighed 0.1820 grm. The entire dilution was 125 c.c. With a second cadmium solution (=0.1057 grm. Cd) together with the same quantity of zinc as before, 20 c.c. Na_2HPO_4 (sp. gr. 1.0358), 3 c.c. H_3PO_4 (sp. gr. 1.347), and 100 c.c. water, 0.1060 grm. cadmium was obtained. This deposit was crystalline, but in spots slightly spongy, which may account for its being somewhat higher than the theoretical. Two more separations of these metals were made, with a reduction of the phosphoric acid from 3 c.c. to 2 c.c., otherwise the conditions remained as before, and the cadmium obtained was in (a) 0.1057 grm. and in (b) 0.1051 grm. The current strength in these depositions was 0.37 c.c. oxyhydrogen gas per minute in each dish. *b* is low; its filtrate gave a trace of cadmium sulphide upon testing with hydrogen sulphide. My experience has been that in experiments such as these it should never be omitted to increase the current for about one hour previous to the final disconnection.

Cadmium from Nickel.

Only two experiments were made with these metals. They were conducted in the same manner as those with zinc and cadmium. The cadmium found was in (a) 0.1059 grm., and in (b) 0.1051.

* American Chemical Journal, ii., 41.

Cadmium from Iron.

The quantities of the metals were 0.1700 grm. iron and 0.1057 grm. cadmium. The alkaline phosphate and phosphoric acid were the same as with cadmium and zinc. Total dilution, 100 c.c. Current, 0.37 c.c. oxyhydrogen gas per minute. The deposited cadmium weighed in (a) 0.1058 grm. and in (b) 0.1062 grm.

Cadmium from Chromium.

In this separation the conditions were the same as with the preceding metals. Found cadmium was 0.1055 grm. The deposit was spongy, and the reduction of the strength of the current seemed not to remove this undesirable feature.

Cadmium from Aluminium.

The quantity of cadmium present was 0.2120 grm., while the aluminium was in equal amount. The alkaline phosphate, free phosphoric acid, total dilution, and current strength were the same as with zinc and iron. The results obtained were in (a) 0.2122 grm. Cd and in (b) 0.2120 grm. Cd.

The separation of copper from the metals mentioned in connection with it was not attended by any difficulty whatever, but with cadmium, compliance with the conditions mentioned was absolutely required, otherwise the results varied. In solutions containing free phosphoric acid, cadmium is unusually inclined to sponginess, so that concentration of liquid should be avoided, and the poles of the acting battery should not approach too closely to each other. The most favourable separation was found to be $\frac{1}{2}$ inches and the proper dilution of the liquid 100–150 c.c. Such, at least, was the case in the separations just described.

Copper from Cadmium.

These metals have been separated from each other in the presence of free nitric acid,* and also in the presence of free sulphuric acid.† From the results about to be given, their separation in the presence of free phosphoric acid is also possible. Two experiments were conducted under the following conditions:—0.2452 grm. copper as sulphate, 0.1827 grm. cadmium as sulphate, 20 c.c. Na_2HPO_4 (sp. gr. 1.0358), and 10 c.c. H_3PO_4 (sp. gr. 1.347), with a total dilution of 125 c.c., were exposed to the action of a current generating 0.10 c.c. oxyhydrogen gas per minute for a period of twelve hours, when the following amounts of metallic copper were obtained:—in (a) 0.2451 grm. and in (b) 0.2452 grm. In a third experiment, with double the amount of copper present, the current was allowed to act through the night, and the deposited metal weighed 0.4904 grm. Again, with a current liberating 0.2 c.c. oxyhydrogen gas per minute, conditions in all other respects similar to those previously mentioned, the found copper was 0.2451 grm. Cadmium was not detected in these deposits. The filtrates showed no trace of copper.

Silver phosphate is readily dissolved by phosphoric acid, but from such solutions even the feeblest currents deposit the metal in a spongy condition, so that it was useless in the quantitative work. But from an ammoniacal solution of the phosphate the deposition of silver metal is quite rapid and satisfactory. Two experiments gave, with a current liberating 0.20 c.c. oxyhydrogen gas per minute, in (a) 0.1065 grm. and in (b) 0.1061 grm. Ag, the required being 0.1062 grm. Ammonia just sufficient to dissolve the phosphate is all that should be used. As I have not observed this mode of depositing silver described in the literature of electrolysis I include it here, although it is only to the department of acid phosphate solutions that I wish to direct attention. The behaviour of lead phosphate in alkaline solution has

been recorded by me.* The results given are quite satisfactory. As already remarked, its phosphate being insoluble in phosphoric acid excludes experimentation in that direction.

One of the most interesting observations made in this study of acid phosphates and the electric current is that with manganese. It is well known that from nitric or sulphuric acid solution this metal is deposited as dioxide by the current. In the presence of phosphoric acid, where there is a decided excess of the latter, the deposition of dioxide upon the positive pole does not take place. This behaviour has enabled me to present the following separations of copper from manganese:—

1. 0.1770 grm. copper as sulphate, 0.1500 grm. manganese as sulphate, 30 c.c. Na_2HPO_4 (sp. gr. 1.0358), 10 c.c. H_3PO_4 (sp. gr. 1.347) with a total dilution of 120 c.c., were exposed to the action of a current giving 1 c.c. oxyhydrogen gas per minute. Copper found equalled 0.1765 grm.

2. The conditions the same as in (1), except that the current gave 1.4 c.c. oxyhydrogen gas per minute. Found copper weighed 0.1770 grm. The positive pole showed no dioxide deposition. When the current exceeded that given in (1) and (2) a pink colouration was observed about the anode. This non-precipitation of the manganese is very likely due to the formation of the phosphate of the sesquioxide, which is only decomposed, and then but partially, by much more powerful currents than were used in this separation.

The behaviour of other metallic phosphates in acid solution is receiving attention in this laboratory.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

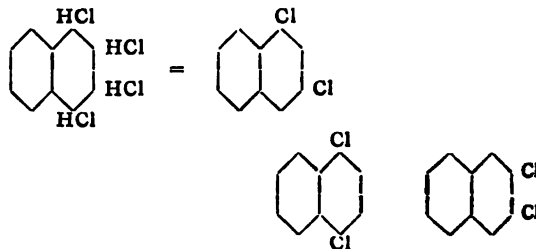
Ordinary Meeting, May 15th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

(Concluded from p. 275).

39. "The Chlorides of Naphthalene and its Derivatives, and the Manner in which they are Decomposed by Alkalies." By HENRY E. ARMSTRONG and W. P. WYNN.

It being established that 1-dichloronaphthalene is the homo- $\beta\beta$ -modification, it follows that naphthalene tetrachloride affords the three theoretically possible dichloronaphthalenes.



The 1:3 compound is produced in largest, the 2:3 in smallest, quantity.

Hitherto it has always been supposed that the dichloride which is the initial product of the interaction of naphthalene and chlorine decomposes only in one way, yielding α -chloronaphthalene; the authors find that β -chloronaphthalene is also produced. They have been led to this discovery by further study of the isomeric acid obtained in small quantity together with 1:4 chloronaphthalenesulphonic acid from α -chloronaphthalene by Armstrong

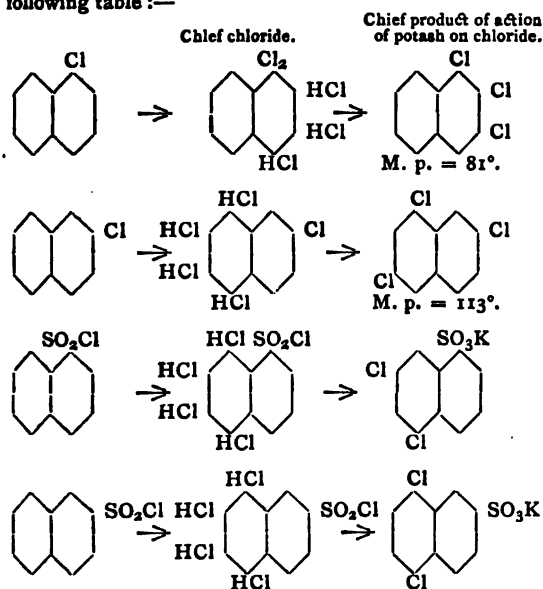
* American Chemical Journal, ii., 42.

† Ibid., xli., 110.

* Proceedings Am. Phil. Soc., 1897.

and Williamson (*cf. Proc. Chem. Soc.*, 1886, 233; *B. A. Report*, 1887); this acid proves to be identical with that obtained on sulphonating β -chloronaphthalene. In like manner, the secondary product obtained by Armstrong and Williamson from bromonaphthalene is derived from β -bromonaphthalene, which is present in ordinary bromonaphthalene even after considerable fractionation. The proportion of β -compound produced is but small in either case. This recognition of the presence of the β -compound in bromonaphthalene affords an explanation of Jolin's observation that the sulphonation product of bromonaphthalene contains an acid convertible into 2:3' dibromonaphthalene.

The manner in which chlorine acts on derivatives of naphthalene, as well as that in which the resulting chlorides decompose, becomes of special interest now that Bamberger's researches have shown how very differently the α - and β -derivatives behave when hydrogenised; in the course of their experiments the authors have had occasion to collect a number of data bearing on this question, having re-examined the action of chlorine on the two chloronaphthalenes and the two monosulphochlorides. In each case chiefly one tetrachloride is formed, and this decomposes chiefly in one way, the amount of subsidiary products in either case being relatively small; the exact nature of these subsidiary products has yet to be determined, and cannot be ascertained until considerable quantities of material have been operated on, and a more exact knowledge of some of the trichloronaphthalenes has been obtained. The results of their own and previous observations are summarised in the following table:—



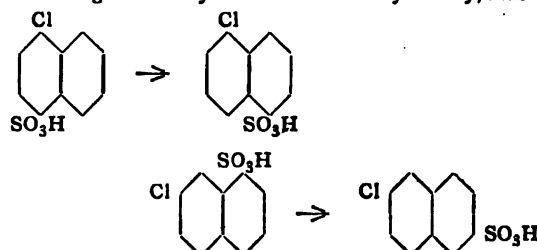
The influence of the substituent, both as affecting the addition of chlorine and the elimination of hydrogen chloride, is especially noteworthy. It will be seen that the sulphochlorides behave alike, but the two chloronaphthalenes dissimilarly towards chlorine, and that each compound decomposes in a manner peculiar to itself on treatment with alcoholic potash.

40. "Isomeric Change in the Naphthalene Series, No. 6. The Influence of Position in Determining the Nature of the Isomeric Change in the Case of the Mono- and Dichloronaphthalenesulphonic Acids." By HENRY E. ARMSTRONG and W. P. WYNNE.

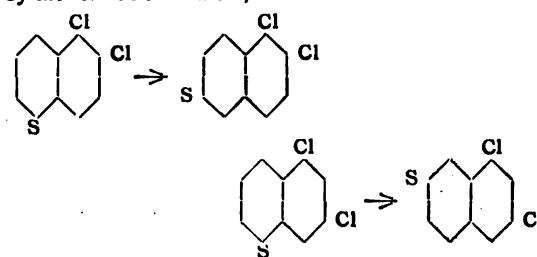
Arnell, in an "academic treatise" ("Bidrag till Kannedom om Naftalins Chlorsulfonylor," Upsala, 1889), in which a valuable summary is given of all that

was known of the subject at the time of its publication, states that when α -chloronaphthalene is sulphonated by means of sulphuric acid, it yields both the 1:4- and the 1:4'-derivative, the latter forming a large proportion of the product when the sulphonation is effected at an elevated temperature (160°). The formation of the 1:4'-acid when sulphonation was effected by means of chlorosulphonic acid was overlooked by Armstrong and Williamson, but the experiments which they made on the effect of heating the initial product (these *Proceedings*, 1887, 145) led them to believe that the 1:4-acid was converted into the 1:4'-isomeride. Further study of the subject has shown that the 1:4'-acid is obtained in small quantity when a cold solution of α -chloronaphthalene is sulphonated by means of SO_3HCl , the product being heated only for a short time on the water-bath to remove the bisulphide; and that if the product be heated at about 150° during five to six hours, almost complete conversion into the 1:4'-acid is effected. It is, therefore, not improbable that the 1:4-acid is the only immediate product of sulphonation, and that the small quantity of the isomeride obtained at low temperatures is due to the occurrence of isomeric change at the moment of inter-action.

The fact that the α -chloronaphthalene-derivative undergoes change into the more symmetrical α -isomeride, while 2:1'- β -chloronaphthalenesulphonic acid is converted in a similar manner into the more symmetrical β -isomeride, appears to be noteworthy as indicating a tendency to a final state of symmetry, thus—



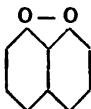
On reference to the tables on p. 274, in which the constitution of the acids formed on sulphonating the ten dichloronaphthalenes is indicated, it will be observed that in some cases an α - and in some cases a β -sulphonic acid is formed or a mixture of both. The authors are of opinion that the α -acid is always initially produced; in some cases this is so unstable that it spontaneously passes over into the β isomeride and escapes observation, while in others it is partially preserved. They base this conclusion on the fact that in all cases hitherto studied in which both acids are formed it is possible to convert the α - into the β -acid by heating. Thus 1:2 dichloronaphthalene affords about two-thirds α - and one-third β -acid, but when the product is heated the latter is practically the sole product (*cf. B. A. Report*, 1889). In like manner the product of initial sulphonation from 1:3 dichloronaphthalene contains about one-fifth β -acid; but if this be heated at 160° during 18 hours, complete conversion into the β -isomeride is effected. It is noteworthy that the position ultimately taken up by the SO_3H radicle appears to be determined by the β -chlorine atom, thus—



The β -sulphonic acids are probably the most "degraded" products, and from this point of view the further study of the behaviour of the 1:4'- α chlorosulphonic acid and of the 1:1':4- $\alpha\alpha$ dichlorosulphonic acids, as well as that of the 2:1' and 2:4'- $\alpha\beta$ - and 2:3 and 2:3'- $\beta\beta$ -dichlorosulphonic acids, will be of special interest, in order to ascertain whether or no the determining factor is the tendency of the molecule to acquire a configuration which most nearly approaches symmetry.

41. "A Third Naphthaquinone." By R. MELDOLA, F.R.S., and F. HUGHES.

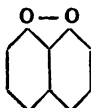
In preparing monobromindone by the action of fuming nitric acid on dibrom- α -naphthol (*Proc. Chem. Soc.*, 1890, 57), a small quantity of a by-product is obtained which remains undissolved in alcohol on treating the crude indone with this solvent; a sufficient quantity of this substance has been obtained by the authors to enable them to identify it as a new naphthaquinone. The pure substance forms slender pale yellow needles, having no distinct melting-point, but blackening about 220°. It is not reduced by sulphurous acid solution, but by treatment with zinc-dust and acetic acid it is converted into a dihydroxynaphthalene crystallising in whitish needles which become slate-coloured on exposure to the air and have no definite melting-point, but darken about 205°. The dihydroxynaphthalene has all the properties of a phenol, and is readily re-converted into the quinone by oxidation. Its diacetyl derivative fuses at 226–227°. On oxidation with alkaline permanganate it affords 1:2:3 hydroxyphthalic acid, $C_6H_4(CH)(COOH)_2$ (m. p. 194–197°), and hence the authors conclude that the quinone is the unknown peri-derivative:—



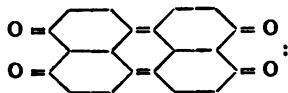
The formation of this quinone during the oxidation of dibrom- α -naphthol by nitric acid cannot at present be explained; but the authors suggest that in the bromination of α -naphthol a minute quantity of peri-monobrom- α -naphthol is produced, and that this is converted into the quinone by the action of nitric acid. Experiments to test this explanation are in progress.

DISCUSSION.

Dr. ARMSTRONG said it appeared to him that, regarding the quinones as diketones, four true quinones could not be derived from naphthalene; the new compound described by the authors either had the constitution indicated by the formula which they had suggested,—



or it was a keto-compound of higher molecular weight, viz.:—



Judging from its properties, this latter explanation appeared the more probable. It would, perhaps, be possible to decide this question by means of the Raoult method. The compound was of a novel type, and was one of great interest. The speaker also expressed the opinion that the formula assigned to the bromindone anilide which Professor Meldola had exhibited (*Chem. Soc. Trans.*, 1890, 399) did not satisfactorily account for its colour.

Dr. QUINCKE drew attention to Graebe and Veillon's experiments on the oxidation of acenaphthalene, and his own on nitroperinaphthaquinone; he thought that the

compound obtained by the former chemists was the quinone now described by Professor Meldola and Mr. Hughes.

Mr. GROVES, in reference to Dr. Armstrong's statement that the new substance was not a true quinone, remarked that the same had been said of β -naphthaquinone at the time of its discovery; it was a quinone notwithstanding. The new quinone, certainly, like dinaphthyl- β -diquinone, was very sparingly soluble in most solvents; but, on the other hand, it could easily be obtained in well-formed crystals, whilst the diquinone was a crystalline powder.

Professor MELDOLA stated that the limitation of the term quinone to such compounds as could be represented as diketones was quite arbitrary, and he thought it justifiable to apply the name to all four dioxy-derivatives of naphthalenes indicated by theory. It was for a long time undecided whether the quinones were peroxides or diketones, and even now the question could not, in his opinion, be regarded as definitely settled. He did not think the alternative formula suggested by Dr. Armstrong was more probable than their own, but the decision of the question by Raoult's method would be attempted, although he feared the extreme insolubility of the compound in most solvents would interpose great practical difficulties. The objection raised against the formula of bromindone anilide was of too general a nature to be met, especially in the absence of any alternative suggestion. He was not aware that any chemical formula could be written so as to account for the colour of an organic compound. It was well known that all the anilides of quinone were highly coloured bodies, and the formula proposed was the only one which satisfactorily represented the formation and properties of the compound in question. With respect to Dr. Quincke's observation, Professor Meldola expressed his acquaintance with the work referred to, and stated that reference had been made to it in their paper (*Chem. Soc. Trans.*, 1890, 398). The compound described by Graebe and Veillon had had the formula $C_{24}H_{14}O_2$ ascribed to it by those authors (*Ber.*, 1887, 659).

42. "The Relative Antiseptic Powers of Isomeric Organic Compounds." By THOMAS CARNELLEY, D.Sc., Aberdeen, and W. FREW, Dundee.

The authors have determined the relative antiseptic powers, in reference to ordinary aerial micro-organisms, of a number of isomeric organic compounds, more particularly di-derivatives of benzene, with the object of investigating the influence of atomic arrangement on this property.

A table of results is given which indicate that, so far as the compounds which have been tried are concerned (and with the exception of the hydroxybenzoic acids), para-compounds are more antiseptic than the corresponding ortho- and meta-compounds. On the whole, compounds containing the carboxyl-group are comparatively weak, while phenols and nitro-compounds are relatively strong antiseptics; paranitrophenol being, with the exception of α -naphthol, the most powerful of any of the compounds tried. These results entirely accord with those of Wolcott Gibbs and Hare, who have recently investigated the poisonous action of di-derivatives of benzene on dogs.

43. "Note on the Preparation of Pyrocatechol." By W. H. PERKIN, Jun., Ph.D.

The very high price of pyrocatechol renders it desirable to discover improved methods of preparing it; the author has, therefore, studied the action of iodic acid on guaiacol, which is easily procured at a moderate cost. He finds that an almost theoretical yield of pyrocatechol may be obtained by boiling guaiacol with a fuming solution of hydrogen iodide; details are given in the paper.

44. "Benedikt's Acetyl Values." (Second Notice). By J. LEWKOWITSCH, Ph.D.

The results quite recently brought forward by the author (*Proc. Chem. Soc.*, 1890) were so unexpected that it was determined to verify them by examining other fatty

acids; capric, lauric, and cerotic acids were therefore acetylated in the manner previously stated. The approximate purity of the acids used was ascertained by determining the quantity of caustic potash required for their saturation.

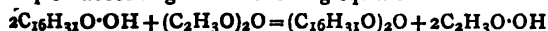
Capric Acid.—The acid value was found to be 318.65, while theory requires 326.2. The acetylated product gave an acid value of 176.4, and a saponification value of 350.4; consequently an acetyl value = 174.

Lauric Acid.—The acid value found was 273.02, the theoretical value being 280.5. The acetylated acid gave an acid value = 161.5, a saponification value = 293.99; its acetyl value therefore was 132.49.

Cerotic Acid.—The acid value found was 128.4; theory indicates for $C_{26}H_{52}O_2$ 141.6 (or for $C_{27}H_{54}O_2$ 136.8). The acetylated cerotic acid gave an acid value = 73.87, a saponification value = 142.1; so that the acetyl value was 68.23.

From the approximate coincidence of the acetyl value of capric acid (174) with the acid value of the acetylated acid (176.4), it might be inferred that the acetylated capric acid contains one acetyl-group, but an acid of the formula $C_{20}H_{40}O_2 \cdot C_2H_5O$ has a theoretical acid value of 262. Similarly, the value for a mono-acetyl derivative of lauric acid would be 231, and that for a mono-acetyl derivative of cerotic acid 128 (resp. 124). (The same formulæ would apply to mixed anhydrides of acetic acid and capric acid, &c.). It was easy to decide whether the action of acetic anhydride on fatty acids affected the COOH-group of the latter, for in that case an alcohol of the $C_nH_{2n+2}O$ series ought not to become acetylated. The author experimented on cetyl alcohol, which was treated with acetic anhydride. The acid value of the resulting substance was—as is to be expected—nil; the saponification value found was 192.65. As a substance of the formula $C_{16}H_{33}O \cdot C_2H_5O$ has theoretically a saponification value = 198, it is evident that simply etherisation of the cetyl alcohol has taken place.

It was therefore to be supposed as the mixed anhydrides of the higher fatty acids and acetic acid could not have been formed, that by the interaction of acetic anhydride and the higher fatty acids the anhydrides of the latter had been produced—taking palmitic acid as an example—according to the following equation:—



In that case the quantities of caustic potash required by the equation $(C_{16}H_{31}O)_2O + 2KOH = 2C_{16}H_{31}O \cdot OK + H_2O$ ought to agree with the saponification values found. The following Table gives the quantities of caustic potash required by theory, in m.grms, compared with the quantities actually used in the above experiments:—

	Mol. wt.	Theory.	Exper.
Capric anhydride, $(C_{10}H_{19}O)_2O$..	326	344	350.4
Lauric anhydride, $(C_{12}H_{23}O)_2O$..	242	294	293.99
Palmitic anhydride, $(C_{16}H_{31}O)_2O$..	494	227	226.13
Stearic anhydride, $(C_{18}H_{35}O)_2O$..	550	204	221.18
Cerotic anhydride, $\left\{ \begin{array}{l} (C_{26}H_{51}O)_2O \\ (C_{27}H_{53}O)_2O \end{array} \right.$	774	145	142
	818	137	
Oleic anhydride, $(C_{18}H_{33}O)_2O$..	546	205.4	242

Considering the approximate purity of the acids used, the theoretical values agree very well with the experimental values; and it may be pointed out that with pure material it would be easy by this method to determine which is the formula of cerotic acid.

In the light of this explanation, the "acid values found for the products of the interaction of acetic anhydride and fatty acids lose every quantitative meaning; these values have only been found as the "acetylated" acids were dissolved in cold absolute alcohol for titration with potash, which hydrolysed at once the anhydrides; hydrolysis ceasing only when a limit is reached which depends on the quantity of alcohol present, and the nature and dilution of the standard solution, in some experiments half normal soda, in others decinormal potash. Had the

substances been shaken up with water (hot water does not decompose them), on the first drop of potash falling into the mixture the pink colour would have appeared at once, or very soon, when the limit for the system of substances was reached. It is hardly necessary to state that experiments carried out in this direction fully bear out the correctness of the author's conclusions. Thus the interaction of KOH or NaOH and the anhydrides in aqueous solution affords an elegant illustration of that class of actions which require a measurable time for their completion. The anhydrides of the higher fatty acids are now within easy reach, as they can be prepared in a very short time by means of acetic anhydride.

PHYSICAL SOCIETY.

June 16, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

MR. H. TOMLINSON, F.R.S., read a paper on "*The Effect of Change of Temperature on the Villari Critical Points of Iron.*"

This, he said, was a continuation of the paper he read before the Society on March 21, and the method employed was the same as then described (see *Phil. Mag.*, vol. xxviii., p. 394). Since then, however, he has made experiments at various temperatures up to 285° C., the temperature being determined from the resistance of a platinum wire whose temperature coefficient was carefully determined. The following table shows some of the results obtained with a well annealed iron wire 1 m.m. in diameter, which had been repeatedly heated up to 300° C. and cooled to the temperature of the room until the temporary permeability with various loads attained constant values at both temperatures:—

Magnetising Force in C.G.S. Units.	Load in kilograms, for which permeability is the same as for unloaded wire at temperature—				
	12° C.	76° C.	167° C.	244° C.	285° C.
2.84	4.7	5.0	5.3 and 12	5.7 and 10	None.
3.70	2.5	3.2	3.6	4.2	11.5 4.7 and 9.9
4.8	1.8	2.5	2.7	—	3.1 " 12.3
7.69	None.	None.	None.	None.	None.
10.40	"	"	"	"	"
15.32	"	"	"	"	"

Curves from which these numbers were obtained are given in the paper, and in these load in kilograms and percentage change of temporary permeability are plotted. From the curves and Table it was seen that if the first points in which the curves cut the load line be considered, then at all temperatures the Villari values increase as the load decreases. If, however, the second points be taken, the critical values increase both with load and temperature. In both cases the Villari value is increased by rise of temperature. From the curves it follows that rise of temperature reduces the total variation of permeability producible by loading. A table showing the temporary permeability of the unloaded wire at the various temperatures accompanies the paper.

A paper "*On the Diurnal Variations of the Magnet at Kew*," by W. G. ROBSON and S. W. J. SMITH was communicated by Prof. Rücker.

In some preliminary remarks the Professor pointed out the great advisability of having the results of magnetic observations at various observatories reduced and published in the same manner and for the same periods. In order that this may be effected the methods of reduction must be reliable but not very elaborate. The Greenwich plan is too laborious to be generally adopted, but the method suggested by Dr. Wild (*Rep. Brit. Ass.*, 1885, p. 78), in which the mean diurnal variation is obtained from measurements on five quiet days in each month, is feasible. With a view to further testing the reliability of this method the work described in the paper was under-

taken. Mr. Whipple had made a comparison of the two methods for the years 1870—71—72, with the result shown in the following table:—

$$K_s - K_w = 0.7' \text{ (minutes of arc)}$$

$$G - K_s = 1.2'$$

$$G - K_w = 1.6'$$

Where K_s is the mean diurnal range at Kew as obtained by Sabine's method.
 K_w the mean diurnal range at Kew as obtained by Wild's method.
And G the mean diurnal range at Greenwich by the Greenwich method.

He also found that the mean hourly differences followed some definite law.

The authors undertook the reduction of the Kew observations according to Wild's method for the years 1883, 1886—87; the first was chosen as being a year of maximum sun spots. The results give:—

$$\begin{array}{llll} 1883.. & .. & G - K_w = 1.5' \\ 1886.. & .. & " & = 1.2' \\ 1887.. & .. & " & = 1.9' \end{array}$$

There is thus a difference of nearly two minutes in the variations at the two places, and this cannot all be accounted for by the method of reduction. Another peculiarity is that the range, as calculated by Wild's method, is greater by about 0.5' than that obtained by Greenwich method, although the latter includes days of moderate disturbance. The total range at both places has diminished by about 1.6' between 1883 and 1887. The paper is accompanied by tables and curves plotted from the differences in the mean hourly readings at Greenwich and Kew for each of the above six years, and a marked similarity exists between all of them. The mean of the six curves differs in no case by more than 0.4' from the curve for any year. It is thus possible to calculate the Greenwich values from the Kew numbers, and as these latter are published about two years sooner than the former, this fact may be very important.

Referring to the reduction of results, Prof. RÜCKER said that the Stonyhurst observers and Prof. Mascart were willing to adopt Wild's method; Falmouth, he hoped, would follow suit, and Greenwich had been asked to publish their results in both ways.

Mr. WHIPPLE said that before recording instruments were available, and the numbers were obtained from separate experiments, the labour involved was considerable, and a single large disturbance or magnetic storm might vitiate the result of a whole year's work. Methods were therefore adopted to eliminate these disturbances; of these, that used by Sabine may be particularly mentioned. Although declination records have now been obtained for a considerable number of years, the cause of the variations still remains unknown. They do not seem to be dependent on temperature or on astronomical facts. He considered it valuable to obtain magnetic data from different parts of the earth, but comparisons were only possible when all are published on the same plan. This, he hoped, would result from the efforts of Professors Rücker and Adams. When this is accomplished, the observations on magnetic force will need treatment; the work will be laborious, and the aid of volunteers like Messrs. Robson and Smith would be of great service.

Prof. W. G. ADAMS said he was glad to see the satisfactory nature of the work which had just been brought before the Society. Usually, the mass of figures to be dealt with was so large that the mere reduction was a great undertaking. If, however, the difference between results obtained by the Greenwich and Wild's method was not more than 0.4', it may be possible to make out the causes of the variations from observations reduced on Wild's plan. He himself would put more faith in

horizontal force observations, and wished they could be worked out by some ready method. He hoped the one adopted in America, of obtaining mean curves by photography, may prove satisfactory.

Prof. PERRY asked if a machine could not be made to do the work.

Mr. WHIPPLE said such machines had been used by the Meteorological Office, but they were so elaborate and expensive that clerical work was just as cheap. The method of photographing mean curves had been tried at Kew, but it was open to the objection that accidental disturbances such as those produced by the movement of iron in the vicinity and the approach of cabs, &c., were not eliminated.

Mr. BOYS referring to the use of integrators, said that for a harmonic analyser his disc-cylinder pattern was preferable to the ball disc-cylinder integrators of J. Thomson, for it is much cheaper and has less inertia.

The PRESIDENT said the movement initiated by Prof. Rücker would be of great service if it resulted in the numbers obtained at the various magnetic observatories being published in the same way. It was a great advantage to have such men, who were not permanently attached to an observatory, to take up the subjects and suggest improvements. The heads of such institutions were usually too much employed in making the necessary reductions to have time for devising improved methods. In his opinion greater freedom should be allowed to the chiefs of observatories, for it should be borne in mind that the object of observations is not to produce volumes of figures but to increase our knowledge.

Referring to the reduction of observations, he thought the voluntary services of senior physical students should be more generally accepted, and to this end he suggested that properly recommended persons should be allowed to spend some time in observatories as honorary assistants. This would be of great use to the students themselves and an advantage to the observatories, for the reduction of observations could then be expedited. As regards the accidental disturbances referred to by Mr. Whipple, he contended that regulations should be adopted to render them impossible.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, June 2, 1890.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—

C. J. Cullingworth, M.D., F.R.C.P.; Jonathan Hutchison, F.R.S., F.R.C.S.; Rudolph Messel, Ph.D., F.C.S.; Henry Charles Mylne; and Dan Rylands.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

OBITUARY.

L. SORËT.

WE regret having to put on record the death of the illustrious chemist and physicist, Louis Sorët, who died on May 13, at Geneva, where he held the chair of physics at the University.

The earliest researches of the deceased were in electricity. His study of the laws of electrolysis led him to define the conditions of the production of ozone, and to determine its density and its chemical constitution. He was the first *savant* who succeeded in installing his actinometric apparatus on the summit of Mont Blanc,

where he obtained a series of simultaneous measurements at three different altitudes. In optics, he devised the double prism showing anomalous dispersion, the circular grating giving focal images by diffraction, the improved fluorescent eye-piece, which renders it possible to observe the invisible ultra violet radiations up to their extreme limit almost as easily as the visible rays, finding that the extreme violet transparency is for some bodies one of the most delicate characters of the chemical purity.

In the body then known as erbia, Soret recognised in 1878 a new body which he designated as the earth X, and which he characterised by its absorption-spectrum. He accepted for it, in the sequel, the name "holmium," given by M. Clève.

His death, at the age of sixty-three, cannot but be regretted as premature.

CORRESPONDENCE.

SULPHATES IN NITRIC ACID.

To the Editor of the Chemical News.

SIR,—I have recently been a good deal perplexed by finding sulphuric acid in steel and pig iron, in which I knew it was not likely to be present, and on careful examination of the acids employed for solution I found that the nitric acid pur., 1.42 s. g., contained a considerable percentage of sulphuric acid. I have used this same make of acid for many years without having any reason to suspect its purity, though only occasionally, for sulphur estimations. The makers have been communicated with by the persons who supply me, and I understand their explanation is that the acid is quite pure as it leaves their factory, and that the sulphuric acid is derived from the bottles in which it is sent out. These are Winchesters of greenish colour, and new ones are always used. The acid of which I am speaking is part of a batch which has been in bottle since last November, and the makers are not surprised at its having picked up sulphuric acid from the bottles. No doubt there is sulphate of soda in the material of which the glass is made, but I find that I can obtain a pure re-distilled nitric acid in bluish-coloured Winchesters which is perfectly free from sulphuric acid, though it has been in bottle about the same length of time as the other. I don't know whether any of your readers have had similar trouble, but I think it may be of value to warn users of so-called pure nitric acid of the necessity of frequently testing it for sulphates, and I should be glad to have information as to the action of nitric acid upon glass bottles in which it is stored, as the present state of things seems to be rather anomalous; viz., that greenish glass Winchesters sometimes contain sulphates capable of being dissolved out by nitric acid, but that bluish glass Winchesters have not been known to contaminate nitric acid in this way; at least, so far as I can ascertain.—I am, &c.,

JAMES H. HUXLEY.

Vickers, Sons, and Co., Limited,
River Don Works, Sheffield,
June 10, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 21, May 27, 1890.

Electro-conductivities of the Compounds of Ammonia and of Aniline with the Oxybenzoic Acids.—D. Bethelot.—The conductivity found experimentally,

contrary to what is observed in the case of the alkaline phenates is always in excess of the mean conductivity. Notwithstanding the difference of the conductivities of the three oxybenzoic acids the conductivity of the mixture is almost the same for the three isomers.

Researches on Dispersion in Organic Compounds (Alcohols of the Fatty Series).—Ph. Barbier and L. Roux.—For the alcohols of the fatty series, which the authors have examined, the dispersive powers are continuous functions of the molecular weights, and, contrary to what takes place for aromatic compounds, the dispersive powers increase at the same time as the molecular weights. The isomeric alcohols with a long chain, primary and secondary, have sensibly the same dispersive power and obey the same laws; only the abnormal primary alcohols studied possess smaller dispersive powers, though their values deviate very notably from that of the alcohols of long chains. The elimination of hydrogen occasions a considerable increase in the dispersive power.

On Homofluoresceine.—E. Grimaux.—The author considers that the trimethylfluoresceine or homofluoresceine of Schwartz is the aurine of orcin.

Justus Liebig's Annalen der Chemie.
Vol. ccliv., Part 2.

Communications from the Chemical Institute of the University of Bonn.—These communications contain memoirs by R. Anschütz and Ferdin. Reuter on the action of aniline upon citraconic acid and itaconic acid; on acetylchlorphenomalic acid, by R. Anschütz; contributions to a knowledge of the monosubstituted succinic acids, by R. Anschütz and Carl Bennert, and an account of the isomerism of fumaric acid and maleic acid by R. Anschütz.

Communications from the Chemical Institute of the University of Halle.—These communications comprise two papers by Hugo Erdmann on the derivatives and transformations of benzallevulic acid and on phenylangelicalacton.

Communications of the University Laboratory of Freiburg.—Papers by W. Autenrieth on the thio-derivatives of the crotonic acids, and by O. Hinsberg and L. von Udransky on some benzoyl compounds.

Communications from the Chemical Institute of the University of Bonn.—Memoirs by R. Anschütz on a new formation of hydantoin and on the preparation of flavan-hydrogen.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 11.

Precipitation of Albumenoids from Urine by Certain Bodies Considered Indifferent.—M. Boymond.—The author, having had considerable difficulty in filtering urine rendered turbid by the presence of bacteria, succeeded in obtaining a perfectly clear bright filtrate by shaking up the sample with talc which had been previously washed, first with hydrochloric acid, then with water, and then dried.

Trichloracetic Acid for the Detection and Determination of Albumen.—M. Boymond.—The author uses this acid in preference to nitric or metaphosphoric acid. It has the advantage of not modifying the albumens. For the separation of globuline, serine, and Patein's variety he determines in one portion of the sample the globuline by means of magnesium sulphate; in another portion the sum total of globuline and serine by ebullition in presence of a few drops of acetic acid. In the filtrate from this precipitate Patein's variety is determined by means of trichloracetic acid.

The Part of Ammonia in the Nourishment of the Higher Plants.—A. Müntz.

Examination of the Sugary Matters extracted from Dates.—L. Grimbert.—Dates contain glucose and levulose, but no saccharose.

Is Potassium Ferrocyanide Poisonous?—P. Carles.—The author points out the harmlessness of potassium ferrocyanide, the sale of which, in some parts of France, appears to be surrounded with red-tape precautions.

Monochloro-camphor obtained by Means of Hypochlorous Acid.—P. Cazeneuve.—These two papers have been already noticed.

MISCELLANEOUS

The Pharmaceutical Society.—At a meeting of the Council of the Pharmaceutical Society, held on the 5th instant, Mr. Michael Carteighe was re-elected President. The Society has just entered its Jubilee year, having been founded in 1841, with the late William Allen, F.R.S., as its first President.

MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Geological, 8.
Meteorological, 7.

THURSDAY, 19th.—Royal, 4.30.
Chemical, 8. Ballot for the Election of Fellows.
"Invertase: a Contribution to the History of an Unorganised Ferment," by C. O'Sullivan, F.R.S., and F. W. Tompson. "The Action of Carbonic Oxide on Nickel," by Mr. Mond and Drs. Langer and Quincke. "The Interaction of Iodine, Water, and Potassium Chlorate," by Henry Bassett. "The Milk of the Gamoose," by A. Pappel and H. D. Richmond.

FRIDAY, 20th.—Physical, 8. "The Stretching of Liquids," by Prof. A. W. Worthington. "The Measurement of Electro-Magnetic Radiation," by C. V. Boys, A. E. Briscoe, and W. Watson. "Notes on Secondary Batteries," by Dr. Gladstone and W. Hibbert.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1595.

ON THE ANALYSIS OF CERTAIN SAMPLES OF TINNED MEAT.

By C. J. H. WARDEN, M.D., Chemical Examiner to Government;
and Assistant Surgeon C. L. BOSE, M.B.,
Assistant Chemical Examiner to Government.

RECENTLY certain samples of tinned meat were examined in the Laboratory of the Chemical Examiner's Department, Calcutta, and the results are perhaps of sufficient interest to be placed on record. The samples were 6-lb. tins of the following brands:—

- 1.—Sydney Meat Preserving Co., New South Wales, Australia Mutton.
- 2.—New Zealand Packing Co., Peach Brand, Auckland Beef.
- 3.—New Zealand Packing Co., Peach Brand, Auckland Mutton.
- 4.—Fairbank Canning Co., Lion Brand, Chicago Beef.
- 5.—Armour Packing Co., Helmet Brand, Kansas City, U.S.A. Beef.
- 6.—Central Queensland Meat Export Co., Rockhampton Beef.
- 7.—Central Queensland Meat Export Co., Rockhampton Mutton.

Before opening the tins their dimensions were taken, and they were weighed with labels intact. The results are recorded in the following Table:—

Description of brand.	Weight (avoir.). lb. oz. gr.	Dimensions in inches and tenths.		
		Height.	Top.	Bottom.
Sydney Meat Preserving Co. Mutton	6 15 50	8.6	4.52 × 4.23	5.1 × 5
New Zealand Packing Co. Beef	6 9 70	8.94	4.9 × 3.7	5.4 × 4.15
New Zealand Packing Co. Mutton	6 14 107	8.94	4.9 × 3.7	5.4 × 4.15
Fairbank Canning Co. Beef	6 14 203	9.2	5.04 × 3.41	5.7 × 4.2
Armour Packing Co. Beef	7 14 202	8.79	5.39 × 4.19	5.41 × 3.7
Central Queensland Meat Export Co. Beef	7 14 105	9.25	4.9 × 3.67	4.14 × 5.37
Central Queensland Meat Export Co. Mutton	7 1 320	9.25	4.9 × 3.67	4.14 × 5.37

All the tins were in a sound condition and free from rust externally. The Fairbank Canning Co.'s tin was coated with transparent blue varnish, and had a small paper label. The New Zealand Packing Co.'s tins were only painted, the nature of the contents being printed in black ink. The remaining tins were painted and also covered with varnished paper labels, except at the top and bottom. We would suggest that in lieu of paper labels the preferable plan of painting and stamping cases of tinned provisions with the brand, nature, and weight of the contents, and year of manufacture. This last point is one which appears to us to be of very considerable moment.

Tinned provisions are, as a rule, chiefly employed when fresh ones are unavailable; and, though tinned meats will

keep for some time, they certainly do not improve by age. As at present put up, one can only roughly judge of their age by the external condition of the tin, a source of information which may obviously lead to very incorrect conclusions.

Out of the seven brands of tinned meat examined by us, only the Fairbank Canning Co.'s sample showed the date of manufacture.

All the tins were larger in area at the base than at the top; an expedient which admits of the contents being readily removed whole.

In the following Table the weights of the empty tins and their contents are recorded:—

Brand.	Weight of empty tin.		Weight of contents.		
	ozs.	grs.	lbs.	ozs.	grs.
Sydney Meat Preserving Co. Mutton	15	33	6	0	16
New Zealand Packing Co. Beef	12	35	5	13	35
New Zealand Packing Co. Mutton	12	393	6	1	151
Fairbank Canning Co. Beef	13	61	6	1	141
Armour Packing Co. Beef	14	35	6	2	167
Central Queensland Meat Export Co. Beef	15	22	6	1	82
Central Queensland Meat Export Co. Mutton	14	341	6	2	417

In the majority of cases the insides of the tins were bright and free from all traces of corrosion or rust.

In chemically examining the samples, the whole of the contents of a tin was in each instance thoroughly well pulped in a large marble mortar, and a portion of the pulped mass used for analysis. Great care was taken to thoroughly scrape the interior of the tins, so as to remove adherent fat and jelly. The tins were then warmed to melt the last traces of fat and jelly, which was also added to the contents of the mortar. The tins were subsequently washed with kerosene oil to dissolve traces of fat, and finally with soap and water, and after drying were weighed. The weight of the contents of a tin being taken as the difference between the weight of a full and empty one. In preparing a specimen of tinned meat for analysis, to merely take a slice and to examine that appears to us to be an erroneous procedure; the contents of a tin must be considered as a whole, and the method we have described of sampling appears to be the only accurate plan by which a knowledge of the general nature of the contents of a tin can be obtained.

In the analysis of an article so prone to decomposition as meat, especially in the tropics, the scheme of examination has to be somewhat carefully considered. We found that certain of the determinations could be made with the meat in the freshly pulped state, while others were preferably made with the desiccated pulp. The first pulp was used for the estimation of moisture, ash, phosphoric acid, chlorine, potash, and soda, and the dried meat for the determination of fat, nitrogen, and aqueous extractive.

For the estimation of moisture five to six grms. of pulp were teased with forceps on the bottom of a flat platinum dish, and exposed at first to a temperature of 100° C., and subsequently to 120° C. in a hot air-bath. The samples were moistened once with absolute alcohol after having been heated for some hours, and the heating continued. Desiccation occupied from eight to nine hours. In another large platinum capsule 30 or 40 grms. of pulp were similarly heated, and when crisp reduced to fine powder and again heated. The dried pulp was preserved in a well stoppered bottle, and used for the determinations already mentioned.

In determining ash,* the portion of the pulp used for

* The samples were examined for foreign metals—tin and lead—in the majority of cases with negative results.

the estimation of moisture was carbonised below redness, reduced to powder in the dish by a flat nail-headed glass rod, and the carbonaceous powder digested with hot water. The solution was then poured on a small filter, and the residue repeatedly washed with warm water. The filter containing the insoluble residue was then dried, and the particles brushed into the platinum dish, which was heated until the whole of the carbon had been consumed. The ash was again digested with warm water, and the solution passed through the same filter. The filter paper was again dried, and, finally, ignited in the dish. After deducting the filter ash, the residue represented the insoluble ash of the sample. The mixed filtrates, on evaporation and ignition just short of redness, affording the soluble mineral constituents. The filter-papers were of C. Schliecher and Schüll's manufacture, and had been extracted with HCl and HF. Control experiments were also made by which the total ash was obtained at one operation. In these determinations great difficulty was often experienced in burning off the last traces of carbon, and prolonged ignition was necessary. As will be seen from the following Table, the total mineral matter obtained by adding together the soluble and insoluble ash was, as a rule, a trifle higher than the "total ash" obtained by one operation, but the difference was not so large as might perhaps have been anticipated.

	Sum of soluble and insoluble ash.	Ash by one operation.
Sydney Meat Preserving Co.		
Mutton	1'530	1'31
New Zealand Packing Co.		
Beef	0'991	0'865
New Zealand Packing Co.		
Mutton	0'621	0'75
Fairbank Canning Co. Beef	1'944	1'628
Armour Packing Co. Beef	4'635	4'38
Central Queensland Meat		
Export Co. Beef	1'716	1'7
Central Queensland Meat		
Export Co. Mutton ..	1'605	—

The soluble ash was used for the estimation of soda and potash, by being dissolved in water, and barium chloride, from chloride and ammonia, added successively, and heated for some time; the precipitate was then filtered off, washed, and the filtrate, after the addition of ammonium carbonate and oxalate, warmed for some time on the water-bath, and filtered. The filtrate and washings was then evaporated to dryness, and gently ignited to remove ammonium salts. On adding water to the residue, a trace of insoluble was filtered off, and the filtrate, after the addition of a few drops of HCl, evaporated to dryness with an excess of platinic chloride. This method of treating the ash of meat preparations is essentially the one described by Dr. A. Stutzer.*

In estimating the alkali metals we employed the following indirect method:—

The residue obtained, as described above, consisting of the double sodium-potassium and platinum chlorides, was treated with alcohol and ether in the usual manner, but instead of weighing the potassium-platinum chloride, it was ignited at a low temperature with the filter-paper on which it had been collected, the residue exhausted with warm water, and the solution of chloride of potassium titrated with standard silver nitrate. The alcoholic solution containing the sodium-platinum salt and an excess of platinum chloride was evaporated to dryness in a small beaker, and the residue washed into a platinum crucible. Ammonium chloride was then added in more than sufficient quantity to combine with the platinum, the mixture evaporated to dryness, and the crucible cautiously heated, first without its cover, and then covered. The residue was treated with warm water, and the chlorine estimated with standard silver nitrate. The

two chlorine titrations thus afforded data from which the amount of H_2O and Na_2O in the ash could be calculated. In carrying out this method of estimating the alkali metals, care must be taken not to under or over heat the residues. Intense ignition would entail loss of chlorides; while by under heating, the whole of the double alkali platinum salt would escape decomposition, and on adding water to the contents of the crucible the solution would have a yellowish colour; in which case, it would be requisite to evaporate the solution and again ignite. We did not find it necessary to separate the finely-divided platinum from the solution of the chloride before titration with silver.

(To be continued).

A SIMPLE FORM OF QUICK FILTER.

By JOSEPH TORREY.

THERE have been many good forms devised for a quick filter, and the principal objection to them collectively is that they are too expensive and cumbersome to be given out to every student. The writer has long felt the need of some form which would take little apparatus and cost as little as possible. The following form has recommended itself since its design by the writer about a year ago by its uniformly satisfactory performance under every test:—

A platinum disc, one inch diam., is cut from ordinarily stout foil. This is then perforated by a steel point with small holes, placed about the same as in Cooke's modification of Dr. Carmichael's reverse filtering button. A margin of about 1-16th inch ought to be left unpierced. The disc thus prepared is placed in a funnel, which can be cut off, if desired, so that the disc will be about $\frac{1}{2}$ inch below the rim of the funnel. A small disc of filter-paper about 1-16th inch larger than the disc is now placed in the funnel just above the disc. Water is applied and pressure turned on. The paper at once settles down and makes an air-tight joint at the edge of the disc. The precipitate can now be brought on the paper and washed as usual.

The results are as good as to rapidity as in case of any form of quick filter, and the ease and convenience attending its use will, I hope, recommend it to some chemists.

Laboratory of Iowa College,
Grinnell, Iowa, May 18, 1890.

THE VIOLET FLAME PRODUCED BY COMMON SALT IN A COAL FIRE.

By A. PERCY SMITH, F.I.C., F.C.S.

THE *Journal of the Chemical Society* for June, 1890, contains an abstract from a paper by G. Salet (*Comp. Rend.*, cx., 282, 283), in which my conclusions as to the origin of the above are contradicted and cupric chloride asserted to be the cause. In the first place, M. Salet errs in describing the colour as blue. It may indeed be blue when copper chloride is heated, but all other chlorides produce a violet flame. I am confident that the violet flame is due to hydrochloric acid, and not to copper, for the following reasons (see also *Nature* and *CHEMICAL NEWS*, March—April, 1879):—

The chlorides of ammonium, potassium, sodium, strontium, barium, and mercury all produce the violet colouration when heated on wire gauze or in a porcelain crucible by coal-gas, a spirit lamp, or pure hydrogen. In these experiments no copper was present. The spectrum of the flame is identical with that produced by throwing common salt into a coal fire. In these experiments we have only two elements in common, viz., chlorine and hydrogen. I proved conclusively by other experiments

* *Analyst*, p. 57, 1885.

that neither sulphur nor carbon entered into the reaction, not that I thought they did, but to disprove the assertions of other people.

The violet flame may also be produced by introducing a drop of hydrochloric acid upon a loop of platinum wire into a Bunsen flame, or one of pure hydrogen; but my proof as to its origin rests upon the fact that when pure hydrochloric acid gas is slowly passed into either of the above flames the violet colour is abundantly formed.

The spectrum of this flame may be found mapped in *Nature*, March 27, 1879. Compared with that of a spark in HCl gas it is seen that the lines in the least refrangible portions are identical, but that the fluted bands of the chloride spectrum are absent in that of the gas, which is easily accounted for by the different conditions under which they are produced. The chloride spectrum is the same under all methods of production given above; that is to say, hydrochloric acid gas heated in a flame gives identically the same result as common salt thrown into a fire.

Dartford, Kent.

THE ELECTROMOTIVE FORCE OF METALLIC SALTS.*

By CLARENCE L. SPEYERS.

OWING to the close connection between chemical action and manifestation of electricity, the study of electrical action promises, if it does not solve, at least great assistance towards the solution of the problem, "What is chemical action?" How brilliantly Ostwald's investigations on electrical conductivity of solutions, aided by the dissociation hypothesis of Arrhenius and others, have illuminated chemical phenomena! The darkness surrounding solution,† diffusion, electromotive force between solutions of different concentration, thermo-neutrality, &c., has been dissipated. True, the light may be false and vanish, but it is the first ever shed on questions hitherto so obscure. If, then, the study of one phase of electrical conduction has taught so much, it is not unreasonable to expect something from an investigation of another side, namely the separation of electricity or production of an electromotive force.

Ordinary self-continued chemical changes are accompanied by a loss of energy (appearing in the form of heat), and it is natural to suppose that with proper arrangements all this heat can be converted into a corresponding quantity of electricity. In fact, Sir W. Thomson suggested this view. Experience, however, has shown that such a statement does not express the truth; a correction is required which, by some, is supposed to be caused by secondary reactions; by others, with Helmholtz at the head, to be due to the existence of two states of energy—the free and the bound. Applying thermo-dynamics to reversible cells, Helmholtz obtains an expression representing the difference between the chemical (as measured in heat) and the electrical energies consumed and developed respectively in the cell. Experience tells that now the case is correctly stated from a mathematical point of view; but the chemical explanation still remains to be discovered. How this will be achieved is, of course, at present uncertain, but will it not probably be through the study of the simplest cases in which an electromotive force is produced. At any rate, it was with this hope that the following investigation was commenced, the plan being to measure the electromotive force of solutions of metallic salts and its variation on systematic dilution. The present paper deals with hydrogen and zinc salts of Cl, NO₃, C₂H₃O₂, and SO₄.

Instead of zinc, an amalgam of this metal was chosen for two reasons: first, the surface presented to the liquid might be considered as homogeneous; secondly, a tarnishing of the brilliant surface would readily reveal any secondary reaction due to oxidation or hydration. With very few exceptions, whenever the electromotive force had an abnormal value, an examination of the amalgam showed an alteration of the surface, evidenced either by a dull film or loss of mobility. The apparent exceptions were probably due to such a thin film that an alteration of surface could not be perceived, but nevertheless existed. The anomalous values were sometimes too high, sometimes too low. Observations were suspended when tarnishing was unmistakably shown. Experiments by Lindeck* and others showed that less than 1 per cent of zinc imparted to mercury an electromotive force equal to that of zinc, justifying the substitution of an amalgam containing 1 per cent of zinc. Hydrogen amalgam not being available, a zinc amalgam was also used with the acids. The negative electrode was composed of pure mercury, so as to neutralise, as far as possible, any chance alteration of electromotive force due to a change of surface tension.

The mercury was purified by causing it to trickle through a solution of mercurous nitrate, comparative experiments showing that this method was as effective and far more convenient than heating with concentrated sulphuric acid.

All liquids contained one grm. equivalent in a litre of water, and, whenever possible, measurements were commenced with solutions of this strength. Zinc chloride and sulphate solutions were prepared by dissolving proper quantities in water, but to obtain solutions of zinc nitrate and acetate, other methods were necessary, owing to the formation of basic salts. The former was successfully made by carefully neutralising normal nitric acid with pure zinc oxide, using tropæolin as an indicator. The latter, by double decomposition, between barium acetate and zinc sulphate, titrating the resulting filtrate with potassium ferrocyanide and diluting with the proper quantity of water. In this way one-half equivalent solution of zinc acetate was easily obtained free from any basic salt.

For measuring the electromotive force a capillary electrometer and compensation cells were used. The method has been so fully described by Ostwald‡ that anything more would be superfluous. To evaluate the electromotive force between the binding posts of the resistance box, as well as that of the compensation battery, two Clark cells were constructed according to Lord Rayleigh's directions.§ As no difference could be detected when the two cells were opposed, although the electrometer was sensitive to less than 0.0001 V, their electromotive force was considered equal to 1.435 [1—0.00077 (t—15)] V. At the close of the present series of experiments a slight inequality (0.0001 V) was observable, which, however, could readily be accounted for by a large fluctuation in the temperature of the room during a few cold winter nights, and the Clark cells not having an equal temperature at the time of measurement. Every two weeks the electromotive of the compensation cells was determined, and every day that between the two binding-posts of the resistance box, the latter being measured by the aid of a compensation cell.

The cell containing the liquid to be experimented upon is outlined in the two figures. *b* is a portion of a thick test-tube drawn out and a platinum wire fused through the bottom *d*. This tube, with a capacity of about 15 c.c., contains the solution and amalgam *u*. Another piece of test-tube is drawn out, a platinum wire inserted, and the glass fused around it, at the same time bending the drawn-out portion upward so as to form a cup, *e*, in which a

* *American Chemical Journal*, Vol. xii., No. 4.

† The writer does not admit that any distinctions are to be made between physical and chemical action other than those of degree and convenience. Of course, mechanical action is excluded.

* *Wied. Ann.*, xxiv., 371.

† One grm. equivalent in two litres of water.

‡ *Zeitschrift f. Physikal. Chem.*, i., 403.

§ "Elementary Pract. Physics," Stewart and Gee, II., 482.

globule of mercury can be placed. The platinum wire makes a metallic connection. The piece *c* must be drawn out in such a manner that when the cup is made its orifice is below the surface of the solution contained in *b*. By grinding *c* into *b* a glass stopper is formed, enabling the liquid to be thoroughly mixed after each dilution. Fig. 1 shows *b* and *c* in position; Fig. 2, *c* alone. Four such cells were constructed, enabling duplicate measurements to be made with two solutions at the same time.

The manner of operation was this:—Two pipettefuls of the solution were introduced, and then about 0.25 c.c. of the carefully cleansed amalgam, the stopper inserted, and the tube gently rocked to and fro, care being taken to fill the cup of the stopper with liquid. The cup was then filled with mercury, which displaced the liquid (the stopper being removed for this purpose), and proper connection made with the electrometer. When the electromotive force became constant, the value was recorded, the mercury in the cup tossed out, the liquid gently shaken, a fresh globule of mercury introduced, and another measurement made. If they did not coincide, the

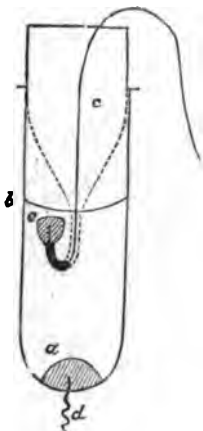


FIG. 1.

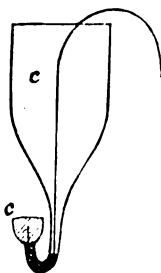


FIG. 2.

process was repeated until a satisfactory agreement was obtained.* Half the liquid being removed, an equal volume of distilled water was added and the above process repeated until the amalgam tarnished. Constant values were often reached in a few minutes with concentrated solutions, but as dilution proceeded a longer interval was required, which in one case (zinc nitrate and sulphuric acid) extended over sixty hours.† Usually, however, twenty-four, but sometimes twelve, hours were sufficient for a series. Now and then the electromotive force would rise and then fall continuously. Under such circumstances the highest value was recorded, justification being found in the fact that no constant value could be obtained by waiting, for the electromotive force decreased continuously throughout a long period of observation. This procedure, however, was only adopted when the highest value of the duplicate was sensibly the same. Such abnormal behaviour was observed only with dilute solutions and concentrated acids—caused in the former case, probably, by a slight alteration of the surface of the amalgam, in the latter by hydrogen evolved from the platinum wire when the latter was exposed to the strong acid while in contact with the amalgam.

The temperature at which the experiments were made was that of the room, about 20° C.

(To be continued).

A METHOD FOR THE DETERMINATION OF IODINE IN HALOID SALTS.*

By F. A. GOOCH and P. E. BROWNING.

(Concluded from p. 281).

IN Series D it appears that the proportion of sulphuric acid increases from 8.3 per cent to 25 per cent of the whole volume before the liquid is found to be free from iodine as such, and even then there sometimes remain minute, though probably insignificant, traces of hydriodic acid.

In the experiment of Series E the liquid was diluted after concentration and the boiling repeated, and the volatilisation of the iodine was thus more nearly perfected than in the corresponding experiments of the previous series—a proportion amounting to 16.6 per cent apparently accomplishing the work done by 25 per cent of the same acid in a single concentration. The results of Series F, G, and H are closely comparable with those of the corresponding experiments of Series D. Throughout these experiments it is again made evident that it is the proportion, and not the absolute amount, of sulphuric acid which is the great factor in the liberation of the iodine. So far as concerns the purpose of good analysis these results indicate the elimination of iodine to a reasonable sufficiency when the reduction of bulk raises the percentage by volume of the strong sulphuric acid to twenty-five, and to perfection, as in the latter determinations of Series G, when the percentage reaches twenty-eight and a half. It remains to be seen whether the arsenious oxide reduced in the separation of the iodine will resist successfully, under the conditions of these experiments, the tendency to volatilise which the presence of chlorides and bromides, and the consequent liberation of hydrochloric and hydrobromic acids, might presumably induce.

The experiments of Series I were directed to the elucidation of this point.

Decinormal solutions of iodine and arsenious acid prepared, standardised, and tested against one another in the usual manner. Definite portions of the solution of arsenious acid were measured from a burette into Erlenmeyer beakers such as were used in the previous experiments, sulphuric acid [1:1] and sodium chloride were added, the volume of the liquid was adjusted to 100 c.m.³ or a little more, and the process of concentration by boiling was carried to the point desired and indicated by a mark upon the flask. After cooling, the acid was neutralised and the titration effected in the usual manner in the presence of an excess of acid potassium carbonate, and starch employed as the indicator. These experiments were arranged upon the presumption that the essential conditions determining the degree of volatility of the arsenic when the reduction is effected by hydriodic acid are imitated, though neither hydriodic acid, nor arsenic acid, nor free iodine is present.

It appears in these results that there is some loss of arsenic in nearly every case within the limits of our experimentation, the amount of volatilisation increasing with the ratio of sulphuric acid to the entire volume when the quantity of chloride present is constant, and likewise with the amount of chloride when the ratio of the acid to the total liquid is constant.

The effect of increasing the amount of chloride is naturally accounted for by the "mass action" of the hydrochloric acid thus liberated upon the arsenious oxide in solution; that it is the proportion, and not the absolute amount, of sulphuric acid which determines the degree of volatility of the arsenic is explicable upon the assumption that the smallest quantity of sulphuric acid employed is sufficient to liberate all the hydrochloric acid (or, at least, nearly all), and that this, by its action on the arsenious

* In a few cases, noted in the tables, satisfactory results could not be obtained.

† For the completed series.

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xxxix., March, 1890.

oxide, forms the volatile chloride proportionately to the amount of water removed bodily by concentration or withheld from effective action by the attraction of the sulphuric acid.

In extending this line of experimentation to cases involving the action of hydrobromic acid upon arsenious oxide we found it sufficient for our purpose to employ only the highest degree of concentration recorded in the previous experiments, and to use 1 gram of potassium bromide—an amount corresponding, molecule for molecule, to about 0.5 gram of sodium chloride. The results, given in Series J, indicate that under these circumstances the loss of arsenic is inappreciable.

It appears, therefore from the results of Series I, that, when the amount of sodium chloride present is restricted to 0.5 gram, the liquid may be boiled until the sulphuric acid amounts to 33.3 per cent of it, with a loss, on the average, of 0.0008 gram of arsenious oxide, and to 25 per cent with a loss of 0.0004 gram. With either of these proportions the results are sufficiently favourable to warrant quantitative testing of a method for separating chlorine and iodine based upon the volatility of iodine and the non-volatility of arsenious oxide under the conditions. The case is even more favourable for the similar separation of bromine from iodine—the loss of arsenic amounting on the average to 0.0001 gram, under similar conditions. The experiments of Series D to H indicated that the degree of concentration at which all iodine vanishes from the liquid corresponds to the presence of 28.6 per cent of the acid—a point midway between the points of concentration indicated above. We fixed this proportion, therefore, for the following experiments, as being rather more favourable as regards the fixity of the arsenic, and perfect as to the elimination of iodine. The smallest absolute amount of sulphuric acid which we have used—10 c.m.³ of the [1 : 1] mixture—demands evaporation of the liquid to a bulk too small to be easily determined with certainty in flasks of the shape and dimensions which we found convenient for this work. The larger amounts of acid are uncomfortably large in the subsequent neutralisation. We took, therefore, 20 c.m.³ of the [1 : 1] mixture of sulphuric acid and water as the amount best adapted to our purpose, and set the limit of concentration at 35 c.m.³.

The potassium iodide which we used was prepared with great care, by adding with re-sublimed iodine upon iron wire, three-fourths of the iodine being added to an excess of iron covered with distilled water, decanting the solution from the excess of iron when the colour of iodine had vanished, adding the remainder of the iodine, pouring the filtered solution slowly into boiling water, to which the exact amount of acid potassium carbonate necessary to combine with the iodine had been added, and filtering off the magnetic oxide of iron thus precipitated. The solution of potassium iodide thus made, very faintly alkaline and entirely free from chlorine and bromine, was made up to a suitable volume and standardised by precipitating the iodine of aliquot portions by weight as silver iodide, which was heated and weighed upon asbestos. Weighed portions of this solution, containing approximately 0.5 gram of potassium iodide to 30 c.m.³, were taken for the tests in which the larger quantities of iodine were introduced; measured portions of a solution made by diluting the former were employed in the tests involving the smaller amounts.

The sodium chloride and potassium bromide used were shown to be free from iodine, and the hydrogen potassium arseniate contained no arsenious acid.

The mode of proceeding was, in general, like that of the previous experiments. The solution of potassium iodide was put in an Erlenmeyer beaker of 300 c.m.³ capacity, 2 grams of hydrogen potassium arseniate were added in solution and followed by 20 c.m.³ of sulphuric acid [1 : 1], the liquid was diluted with water to a little more than 100 c.m.³, a platinum spiral was placed in the flask to secure quiet ebullition, a trap made by cutting off a two-bulb drying tube about an inch from

the inside bulb was hung, large end downward, in the mouth of the flask to prevent mechanical loss, and the liquid was boiled until the level reached the 35 c.m.³ mark put upon the flask. At this point the flask was cooled, the acid nearly neutralised with sodium hydrate in solution, the neutralisation completed by acid potassium carbonate, 20 c.m.³ of the last being added in excess, a definite portion of the starch indicator added, and the contents in arsenious acid determined by titration with a decinormal solution of iodine for the larger amounts, and a centinormal solution for the smaller. Due correction was made for the amount of iodine necessary to develop the test-colour in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodide—the correction amounting to a single drop more of the decinormal solution than was required to produce the end reaction in the same volume of pure water containing only the starch indicator.

The decinormal solution of iodine was made by dissolving 12.65 grams of carefully re-sublimed iodine in potassium iodide (proved free from iodate) and diluting to a litre. The centinormal solution was made by diluting the stronger solution. The standardising was effected by comparison with a solution of arsenious oxide containing 4.95 grams to the litre. This mode of fixing the value of the solution should, and, as the sequel proved, did, indicate the correct standard, but for the sake of confirmation the value of the arsenic solution was re-determined by titration against iodine specially purified by subliming off potassium iodide, re-subliming between watch-glasses, and exposing during forty-eight hours over sulphuric acid. Portions of the iodine thus prepared were weighed in a glass-stoppered weighing-bottle, dissolved in the same without danger of volatilisation by introducing pure solid potassium iodide and a little water, and diluted and treated with the solution of arsenious acid measured from a burette until the colour of iodine vanished. The excess of arsenious oxide was determined by titrating against the standard solution of iodine, whose value in terms of measured portions of the solution of arsenious oxide was perfectly known.

In Series K are detailed experiments which follow the line marked out for the separation of iodine from chlorine and bromine in the haloid salts, excepting that the iodide was entirely omitted for the purpose of discovering whether hydrochloric and hydrobromic acids possess reducing action upon arsenic acid under the conditions. The evidence is plain that no arsenious oxide is formed by the action of 0.5 gram of sodium chloride upon 2 grams of the arseniate under the circumstances as given.

Hydrobromic acid, on the contrary, is slightly decomposed with the evolution of bromine enough to give visible colour to the concentrated liquid, but the amount of bromine lost, as indicated by the arsenious acid produced in its evolution, is only 0.0003 gram for 0.5 gram of potassium bromide, and 0.0001 gram for 0.1 gram of the bromide. Further experiments indicated, however, that concentration cannot go on to a volume less than 35 c.m.³ without causing serious loss when the maximum amount of bromide is present.

In Series L are given the results of twenty-six determinations of iodine by the method outlined.

Upon inspection of these results it appears that the method is good and reliable under all the conditions tested.

When neither chloride nor bromide is present, the iodine is determinable with a mean error of 0.0002 gram.

When sodium chloride accompanies the iodide, the results show a loss of arsenious oxide and a consequent apparent deficiency of iodine—as we should expect in accordance with the indications of Series I. This deficiency proves to be proportional to the amount of iodide broken up, or the arsenious oxide thus produced. For 0.56 gram, approximately, of potassium iodide and 0.5 gram of sodium chloride, the deficiency measured in

Series D.						
KI. Grm.	H ₂ SO ₄ [1:1]. C.m. ³ .	Per cent of strong H ₂ SO ₄ by volume.	H ₂ KAsO ₄ . Grms.	Final volume. C.m. ³ .	Free iodine.	Combined iodine.
0.5	10	8.3	1	60	Present	Abundant.
0.5	10	10	1	50	Present	Abundant.
0.5	10	12.5	2	40	Present	Distinct.
0.5	10	12.5	2	40	Trace	Distinct.
0.5	10	12.5	4	40	Trace	Distinct.
0.5	10	16.6	1	30	Trace	—
0.5	10	16.6	2	30	Trace	—
0.5	10	16.6	2	30	Trace	—
0.5	10	16.6	4	30	None	Distinct.
0.5	10	16.6	5	30	Trace	Distinct.
0.5	10	25	1	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
0.5	10	25	2	20	None	Faintest trace.
Series E.						
0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.
0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.
0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.
0.5	10	16.6	1	{ 30 30 }	None	Faintest trace.
Series F.						
0.5	15	25	2	30	None	Faintest trace.
0.5	15	25	2	30	None	Faintest trace.
0.5	15	25	4	30	None	Faintest trace.
Series G.						
0.5	20	25	2	40	None	Faintest trace.
0.5	20	25	2	40	None	Faintest trace.
0.5	20	25	2	40	None	None.
0.5	20	28.6	2	35	None	None.
0.5	20	28.6	2	35	None	None.
0.5	20	33.3	2	30	None	None.
Series H.						
0.5	30	25	2	60	None	Faintest trace.
0.5	30	25	2	60	None	Faintest trace.
Series I.						
H ₂ SO ₄ [1:1]. C.m. ³ .	NaCl Grm.	Final volume. C.m. ³ .	Per cent of strong H ₂ SO ₄ by volume.	As ₂ O ₃ taken. Grm.	As ₂ O ₃ found. Grm.	Loss. Grm.
{ 10	1	20	25	0.0495	0.0485	0.0010—
{ 10	1	20	25	0.0495	0.0493	0.0002—
{ 10	1	20	25	0.0495	0.0488	0.0007—
{ 10	0.8	20	25	0.0495	0.0488	0.0007—
{ 10	0.5	20	25	0.0495	0.0495	0.0000
{ 20	1	40	25	0.0495	0.0490	0.0005—
{ 20	1	40	25	0.0495	0.0490	0.0005—
{ 20	0.8	40	25	0.0495	0.0490	0.0005—
{ 20	0.5	40	25	0.0495	0.0490	0.0005—
{ 20	0.5	40	25	0.1385	0.1380	0.0005—
{ 20	1	30	33.3	0.0495	0.0476	0.0019—
{ 20	0.8	30	33.3	0.0495	0.0466	0.0029—
{ 20	0.5	30	33.3	0.0495	0.0481	0.0014—
{ 20	0.5	30	33.3	0.0495	0.0485	0.0010—
{ 20	0.5	30	33.3	0.0495	0.0490	0.0005—
{ 20	0.5	30	33.3	0.0495	0.0490	0.0005—
{ 20	0.5	30	33.3	0.0495	0.0490	0.0005—
{ 30	1	60	25	0.0495	0.0485	0.0010—
{ 30	0.8	60	25	0.0495	0.0490	0.0005—
{ 30	0.8	60	25	0.0495	0.0490	0.0005—
{ 30	0.5	60	25	0.0495	0.0490	0.0005—

Summary of Series I.

H ₂ SO ₄ [1:1]. C.m.s.	Final volume. C.m.s.	Per cent of strong H ₂ SO ₄ by volume.	NaCl. Grm.	Mean loss of As ₂ O ₃ . Grm.	Number of determination.
10	20	25	1	0'0006—	3
20	40			0'0005—	2
30	60			0'0010—	1
10	20	25	{ 0'5 and 0'8 }	0'0003—	2
20	40			0'0005—	3
30	60			0'0005—	3
20	30	33'3	{ 0'5 0'8 1'0 }	{ 0'0008— 0'0019— 0'0029— }	{ 5 1 1 }

Series J.

H ₂ SO ₄ [1:1]. C.m.s.	KBr. Grm.	Final volume. C.m.s.	Per cent of strong H ₂ SO ₄ by volume.	As ₂ O ₃ taken. Grm.	As ₂ O ₃ found. Grm.	Loss. Grm.	Mean loss. Grm.
20	1	30	33'3	0'0495	0'0490	0'0005	0'0001—
20	1	30	33'3	0'0495	0'0493	0'0002	
20	1	30	33'3	0'0495	0'0495	0'0000	
20	1	30	33'3	0'0495	0'0495	0'0000	
20	1	30	33'3	0'0495	0'0495	0'0000	

Series K.

H ₂ SO ₄ [1:1]. C.m.s.	H ₂ KAsO ₄ . Grms.	NaCl. Grm.	KBr. Grm.	Final volume. C.m.s.	Iodine correspond- ing to As ₂ O ₃ reduced. Grm.	Chlorine corresponding (average). Grm.	Bromine corresponding (average). Grm.
20	2	0'5	—	35	0'0000	0'0000	—
20	2	0'5	—	35	0'0000		
20	2	0'5	—	35	0'0000		
20	2	—	0'1	35	0'0003	—	0'0001
20	2	—	0'1	35	0'0001		
20	2	—	0'1	35	0'0001		
20	2	—	0'5	35	0'0005	—	0'0003
20	2	—	0'5	35	0'0005		
20	2	—	0'5	35	0'0005		

Series L.

No.	H ₂ SO ₄ [1:1]. C.m.s.	H ₂ KAsO ₄ . Grm.	NaCl. Grm.	KBr. Grm.	Final vol. C.m.s.	KI taken. Grm.	Theory for Iodine. Grm.	Iodine found. Grm.	Error. Grm.	Average error. Grm.
1.	20	2	—	—	35	0'5616	0'4080	0'4079	0'0001—	0'0002—
2.	20	2	—	—	35	0'5630	0'4091	0'4086	0'0005—	
3.	20	2	—	—	35	0'5622	0'4083	0'4086	0'0003+	
4.	20	2	—	—	35	0'0506	0'0400	0'0396	0'0004—	
5.	20	2	—	—	35	0'0506	0'0400	0'0391	0'0009—	
6.	20	2	—	—	35	0'0506	0'0400	0'0400	0'0000	0'0011—
7.	20	2	—	—	35	0'0506	0'0400	0'0401	0'0001+	
8.	20	2	—	—	35	0'0051	0'0040	0'0037	0'0003—	
9.	20	2	—	—	35	0'0051	0'0040	0'0038	0'0002—	
10.	20	2	0'5	—	35	0'5611	0'4077	0'4066	0'0011—	
11.	20	2	0'5	—	35	0'5619	0'4082	0'4073	0'0009—	0'0002—
12.	20	2	0'5	—	35	0'5622	0'4086	0'4073	0'0013—	
13.	20	2	0'5	—	35	0'0506	0'0400	0'0402	0'0002+	
14.	20	2	0'5	—	35	0'0506	0'0400	0'0395	0'0005—	
15.	20	2	0'5	—	35	0'0051	0'0040	0'0037	0'0003—	
16.	20	2	0'5	—	35	0'0051	0'0040	0'0037	0'0003—	0'0008+
17.	20	2	—	0'5	35	0'5619	0'4082	0'4092	0'0010+	
18.	20	2	—	0'5	35	0'5697	0'4138	0'4136	0'0002—	
19.	20	2	—	0'5	35	0'5622	0'4083	0'4099	0'0016+	
20.	20	2	—	0'5	35	0'0506	0'0400	0'0410	0'0010+	
21.	20	2	—	0'5	35	0'0506	0'0400	0'0404	0'0004+	0'0003—
22.	20	2	—	0'5	35	0'0051	0'0040	0'0048	0'0008+	
23.	20	2	—	0'5	35	0'0051	0'0040	0'0049	0'0009+	
24.	20	2	0'5	0'5	35	0'5626	0'4087	0'4083	0'0004—	
25.	20	2	0'5	0'5	35	0'5660	0'4112	0'4111	0'0001—	
26.	20	2	0'5	0'5	35	0'5622	0'4083	0'4079	0'0004—	

iodine amounted to 0.0011 gm. When the potassium iodide is decreased ten-fold (or more) the deficiency falls to 0.0002 gm. It should be recalled, too, in this connection that the results of Series I. pointed to increasing volatility of the arsenic with the increase of the sodium chloride present.

The presence of potassium bromide results in the liberation of minute amounts of bromine and a consequent increase in the arsenious oxide and apparent excess of iodine. The mean error due to this cause is 0.0008 gm. for 0.5 gm. of the bromide, and the variation in the quantity of iodide present is without effect upon it.

The simultaneous action of the chloride and bromide tends, of course, to neutralise the error due to each. Thus, in the mixture weighing about 1.5 grms. and consisting of sodium chloride, potassium bromide, and potassium iodide in equal parts, the mean error amounts to 0.0003 gm. — The largest error in the series is 0.0016 gm. +, when the bromide was at its maximum and no chloride was present; and the next largest was 0.0003 gm. —, when the chloride was at its maximum and no bromide was present.

It is obvious that when the amounts of chloride and bromide present are known approximately it is possible to apply corrections which shall eliminate errors in the indicated amount of iodine due to the action of these substances. From the averages of Series I it is apparent that the amount to be added in each case may be obtained by multiplying the product of the weights in grms. of sodium chloride and potassium iodide by the constant 0.0004; and the amount to be subtracted, by multiplying the weight in grms. of potassium bromide by 0.0016. Thus, for example, the correction in 24 will be 0.0011 gm. + ($= 0.5 \times 0.56 \times 0.0004$) and 0.0008 gm. — ($= 0.5 \times 0.0016$). The individual results of Series I thus corrected will stand as follows:—

No. of Expt.	Theory for Iodine. Grm.	Corrected amount of Iodine found. Grm.	Error. Grm.
1.	0.4080	0.4079	0.0001—
2.	0.4091	0.4086	0.0005—
3.	0.4083	0.4086	0.0003+
4.	0.4000	0.0396	0.0004—
5.	0.0400	0.0391	0.0009—
6.	0.0400	0.0400	0.0000
7.	0.0400	0.0401	0.0001+
8.	0.0040	0.0037	0.0003—
9.	0.0040	0.0038	0.0002—
10.	0.4077	0.4077	0.0000
11.	0.4082	0.4084	0.0002+
12.	0.4086	0.4084	0.0002—
13.	0.0400	0.0403	0.0003+
14.	0.0400	0.0396	0.0004—
15.	0.0040	0.0037	0.0003—
16.	0.0040	0.0037	0.0003—
17.	0.4082	0.4084	0.0002+
18.	0.4183	0.4128	0.0010—
19.	0.4083	0.4191	0.0008+
20.	0.0400	0.0402	0.0002+
21.	0.0400	0.0396	0.0004—
22.	0.0040	0.0040	0.0000
23.	0.0040	0.0041	0.0001+
24.	0.4087	0.4086	0.0001—
25.	0.4112	0.4114	0.0002+
26.	0.4083	0.4082	0.0001—
Mean error			0.0001 gm.—.

The mode of proceeding in the analysis of a mixture of alkaline chlorides, bromides, and iodides, according to this method, may be briefly summarised as follows:—

The substance (which should not contain of chloride more than an amount corresponding to 0.5 gm. of sodium chloride, nor of bromide more than corresponds to 0.5 gm. of potassium bromide, nor of iodide much more than the equivalent of 0.5 gm. of potassium iodide) is dissolved in water in an Erlenmeyer beaker of 300 c.m.³ capacity,

and to the solution are added 2 grms. of dihydrogen potassium arseniate dissolved in water, and 20 c.m.³ of a mixture of sulphuric acid and water in equal volumes, and enough water to increase the total volume to 100 c.m.³, or a little more. A platinum spiral is introduced, a trap made of a straight two-bulb drying-tube cut off short is hung with the larger end downward in the neck of the flask, and the liquid is boiled until the level reaches the mark put upon the flask to indicate a volume of 35 c.m.³. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arseniate by the bromide. On the other hand, though 35 c.m.³ is the ideal volume to be attained, failure to concentrate below 40 c.m.³ introduces no appreciable error. The liquid remaining is cooled and nearly neutralised by sodium hydrate (ammonia is not equally good), neutralisation is completed by hydrogen potassium carbonate, an excess of 20 c.m.³ of the saturated solution of the latter is added, and the arsenious oxide in solution is titrated by standard iodine in the presence of starch.

With ordinary care the method is rapid, reliable and easily executed, and the error is small. In analyses requiring extreme accuracy, all but accidental errors may be eliminated from the results by applying the corrections indicated.

THE SEPARATION AND DETECTION OF Al, Cr, Fe, Co, Ni, Zn, Mn, Ba, Sr, Ca, Mg, K, Na, NH₄.*

By J. S. C. WELLS, Ph.D.

In the following course of analysis I have adopted the plan used in "Fresenius," and as far as the methods are the same have used the text as given in that work.

The division into groups is the same as given by Fresenius, viz.:—1st Group—K, Na, NH₄. 2nd Group—Ba, Ca, Sr, Mg. 3rd Group—Al, Cr. 4th Group—Co, Ni, Fe, Zn, Mn.

1. Take a small portion of the solution to be tested, in a test-tube, observe whether it is coloured or not (Note 1), boil to expel H₂S if present (Note 2), if FeO be present (Note 13) add a few drops of HNO₃ and boil to oxidise it to Fe₂O₃ (Note 3), add a little NH₄Cl, then NH₄OH cautiously, just to alkaline reaction, heat gently, and observe if a precipitate is produced; then add some (NH₄)₂S, no matter whether NH₄OH has produced a precipitate or not.

2. *a. Neither NH₄OH nor (NH₄)₂S produces a precipitate*, pass on to 17, for Fe, Co, Ni, Zn, Mn, Cr, Al are not present (Note 4), nor are phosphates, borates (Note 5), silicates, oxalates (Note 6), or fluorides (Note 5) of the alkaline-earth metals, nor silicic acid originally in combination with other metals.

3. *b. (NH₄)₂S produces a precipitate, NH₄OH having failed to do so*: absence of phosphates, borates (Note 5), silicates, oxalates (Note 6), and fluorides (Note 5) of the alkali-earths, of silicic acid originally in combination with other metals, and also if no organic matter is present of Fe, Al, Cr. Pass on to 5, 6, 7, 12; omit 8, 9, 10, 11.

4. *c. NH₄OH produces a precipitate before the addition of (NH₄)₂S*. The course of proceeding now depends upon whether (a) the original solution is simply aqueous and has a neutral reaction, or (b) the original solution is alkaline or acid (Note 7). In the former case pass on to 5, since phosphates, borates, &c., cannot be present. In the latter case regard must be had to the possible presence of all the bodies enumerated in 2, and also in the presence of organic matter, of the combinations of alkali-earth metals with citric and tartaric acids.

The solution must be tested for these acids, and, if found, the analysis must be carried on according to

* *School of Mines Quarterly*, Vol. xi., No. 3.

scheme for phosphates, &c. See *School of Mines Quarterly*, Vol. x., No. 3).

5. DETECTION OF BASES OF GROUPS 3 AND 4 IF PHOSPHATES, &c., ARE NOT PRESENT.

Mix the solution mentioned at beginning of 1, a portion of which you have submitted to a preliminary examination, with some NH_4Cl (Note 8), then with NH_4OH just to alkaline reaction (Note 9), and then $(\text{NH}_4)_2\text{S}$, until the fluid, after being shaken, smells distinctly of that reagent, shake the mixture until the precipitate begins to separate in flakes, heat gently for some time, and filter.

Keep the filtrate (Note 10), which may contain bases of groups 1 and 2 for examination according to 17. Wash the precipitate with water to which a very little $(\text{NH}_4)_2\text{S}$ (Note 11) has been added, then proceed with it as follows:—Remove the washed precipitate (Note 12) from the filter with a spatula, or by rinsing it with the aid of a wash-bottle through a hole made in the bottom of the filter into a test-tube, and pour over it cold dilute HCl (one part HCl , sp. gr. 1.12, with about five parts of water) in moderate excess.

6. a. The precipitate is not completely dissolved, a black residue being left.

This indicates Co and Ni. This indication is not certain, especially in the presence of much FeS , particles of which may become enveloped in the separated S, and thus be protected from the action of the HCl . Filter and wash.

Examine the filtrate according to 8.

7. Test a small portion of the precipitate in the borax bead, first in the oxidising, then in the reducing flame. If the bead in the oxidising flame is violet whilst hot, and of a pale reddish brown when cold, and turns gray and turbid in the reducing flame, nickel is present; but if the colour of the bead is blue in both flames, and whether hot or cold, cobalt is present. As in the latter case, the presence of nickel cannot be distinctly recognised, examine the remainder of the residue as follows:—Dissolve in HCl and a little HNO_3 , evaporate nearly to dryness, dilute with water, and filter, if necessary, from any particles of S, neutralise carefully with KOH , and then add a solution of KC_y , until the precipitate that first forms is completely dissolved; add a little more KC_y , and then bromine water in considerable quantity, taking care, however, to keep the solution alkaline with KOH . The nickel is precipitated as the black hydroxide $(\text{Ni}_2(\text{OH})_6)$. As the cobalt has already been found by the borax bead, no further test for it is necessary.

8. b. The precipitate dissolves completely (except, perhaps, a little S); absence of Co and Ni, at least in notable quantity.

Boil until H_2S is completely expelled; if iron is present (Note 13), add a little HNO_3 and boil, so as to oxidise it to the ferric state (Note 14), filter if any particles of S remain suspended in the solution, and evaporate nearly to dryness. The course of proceeding now depends on whether the colour of the solution indicates chromium or not.

9. Solution is coloured bluish green or violet, and indicates Cr.

Add Na_2CO_3 to strong alkaline reaction, then bromine-water in excess, heat gently for some time, keeping solution alkaline with Na_2CO_3 , and finally heat to boiling, filter, and wash residue.

a. Filtrate contains Na_2CrO_4 , and possibly $\text{Na}_2\text{Mn}_2\text{O}_8$; the latter is indicated by pink or purple colour of the solution (Note 15). Acidify solution with $\text{HC}_2\text{H}_3\text{O}_2$, and test for Cr with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ —a yellow precipitate proves chromium.

b. Residue contains iron and aluminium as hydroxides, zinc and manganese as carbonates.

Dissolve in least possible quantity of HCl , and treat according to 10.

10. Colour of solution does not indicate Cr.

Neutralise carefully with Na_2CO_3 , dilute and add ex-

cess of $\text{NaC}_2\text{H}_3\text{O}_2$, boil and filter hot, wash precipitate with boiling water. Examine filtrate according to 12.

11. Precipitate consists of iron and alumina as basic acetates. Fuse on platinum with NaKCO_3 and a little KClO_3 (Note 16), dissolve in small quantity of boiling water, and filter.

a. Residue consists of Fe_2O_3 and possibly some alumina that has resisted the fusion.

Dissolve in a little HCl and test for iron with NH_4CyS .

b. Filtrate contains $\text{Na}_2\text{Al}_2\text{O}_4$; acidify with HCl , and then add $(\text{NH}_4)_2\text{CO}_3$ in slight excess—a white flocculent precipitate proves alumina.

12. Filtrate contains zinc and manganese, concentrate solution, add a little $\text{HC}_2\text{H}_3\text{O}_2$, heat to boiling and pass H_2S into it. Zinc is precipitated as ZnS (white) (Note 17), filter.

Filtrate contains manganese, add KOH in excess, a white precipitate turning brown on exposure to the air—Mn. Confirm result by testing in Na_2CO_3 bead in oxidising flame—green bead proves Mn.

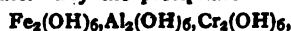
Method using BaCO_3 in place of $\text{NaC}_2\text{H}_3\text{O}_2$.

13. Proceed in the same way as given in 1, 2, 3, 4, 5, 6, 7, 8. In 8, after evaporating nearly to dryness, to expel excess of acid, dilute with water, and neutralise carefully with Na_2CO_3 .

To the neutral solution add BaCO_3 in excess, digest in the cold for some time, filter, and wash. Examine filtrate according to 12 (Note 18).

14. Precipitate contains iron, aluminium, and chromium as hydroxides, together with excess of BaCO_3 . Dissolve precipitate in HCl , add NH_4OH just to alkaline reaction and filter (Note 19).

Reject filtrate. Dry the precipitate—



and fuse in platinum with $\text{Na}_2\text{CO}_3 + \text{KClO}_3$. Dissolve in fusion small quantity of boiling water, and filter.

15. Filtrate contains chromium and aluminium as Na_2CrO_4 and $\text{Na}_2\text{Al}_2\text{O}_4$, divide solution in two parts, a and b.

a. Make acid with $\text{HC}_2\text{H}_3\text{O}_2$, then add a solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ —yellow precipitate—Cr.

b. Acidify with HCl , and then add a slight excess of $(\text{NH}_4)_2\text{CO}_3$ or NH_4OH and boil—white flocculent precipitate—alumina.

16. Residue left after treating fusion with water consists of Fe_2O_3 and possibly some Al_2O_3 . Test for iron by dissolving in HCl and adding NH_4CyS —red colour—iron (Note 13).

(To be continued).

NOTICES OF BOOKS.

Explosives Act, 1875. Fourteenth Annual Report of Her Majesty's Inspectors of Explosives, being their Annual Report for the Year 1889. London: Her Majesty's Stationery Office.

THIS report is in many respects gratifying. We find that the vigilance of the inspectors does not decrease, and that municipal authorities are slowly becoming alive to the importance of the Act and of its execution. The number of fatal accidents in the year was 7, one of them, it is worth noting, in an unlicensed factory. Although the average for the past eleven years was only 7.2, yet the present figure is a substantial improvement, since the number of factories, the average output in each, and the number of hands employed have increased. Hence, unless greater care and intelligence were brought to bear we might naturally expect an increased death-rate. This is the more evident as some new explosives are being introduced where the conditions of safety or danger are not so thoroughly known.

We learn from the Report that a new Chemical Committee has been appointed by the War Office "for the purpose of investigating and dealing with chemical questions relating to explosives for use in the Imperial service." The functions of this Committee are consequently entirely distinct from those of the Inspectors, who have to deal only with the question of public safety in the manufacture, transport, and storage of explosives for civil purposes.

During the year ten new factories have come into existence, the total number under licence being 122, exclusive of "toy firework factories."

One of the accidents, resulting in the death of one man and injuries to three others, took place on October 3 during the unlawful and surreptitious manufacture of Quick-Firing Ammunition by Sir W. Armstrong, Mitchell, and Co. (Limited) on board a barge on the Tyne. This case will yet form the subject of criminal proceedings; hence no comments on the occurrence are made further than a notice of the gross negligence of the Commissioners of the River Tyne, who had allowed this unlicensed manufacture to continue for several months.

Two women—the only persons present at the time—were killed in the packing room of the detonator factory at Polmont, belonging to Nobel's Explosives Company. This accident took place on November 15, and is supposed to be due to the fall of a heavy plate containing detonators upon a similar plate. The two above-mentioned cases and one which took place at Pain's factory, June 4, were the only one which led to official inquiries.

A fatal accident happened in June at the Factory of the Roburite Explosives Company (Limited), near Wigan. The cause of death here was not explosion or fire, but the inhalation of poisonous gases. The victim was cleaning an air-flue into which the fumes of three roburite mixing-pans were discharged. Respirators and other precautions were certainly in use. It is stated that these flues have since been cleaned, when needful, without sending men into them.

One accident—not fatal—led to the detection of an unlicensed and therefore wholly illegal "firework factory," which, as the Report adds, "is not creditable to the local authority."

Some of the accidents in the storage of explosives show gross ignorance on the part of the persons concerned. Thus, at Grangemouth a workman lighted a match "in a store-room in which oil (doubtless mineral oil) and gunpowder were unlawfully kept together." The explosion killed a bystander and injured several persons.

It is remarked that the Act gives the inspectors no power concerning the use of explosives. In an accident due to an improper apparatus used for thawing dynamite the jury recommended the passing of an Act to regulate the use of "high" explosives.

Especial care should be taken by all parties concerned not to leave detonators about. They are sometimes picked up by children who are quite ignorant of their nature.

Cases of malicious attempts against life by means of explosives have not been wanting. On Lord Clanricarde's estate near Woodford, Galway, an infernal machine was arranged in an empty house which it was expected would be entered by the police. The arrangements adopted by the conspirators were essentially identical with those of the infernal machines discovered at Liverpool and Glasgow in 1883, the bombs found on Daly in April, 1884, and the attempted explosion at the Times office in 1883. It is noteworthy that at Woodford the peasantry, instead of crowding round, as at other evictions, had kept entirely aloof.

On September 7 an attempt was made to blow up a house in the outskirts of Tipperary, in which Mr. A. H. Smith-Barry collects his rents.

At Rochdale, on November 29, an attempt was made to blow up the School Board offices. The intended *modus operandi* was to bring sulphuric acid in contact

with potassium chlorate and sugar. The failure, says the Report, "may be referred to a cause which it is not desirable to specify."

As illustrations of modern "progress" in Japan we find that dynamite and dynamitards have penetrated thither also. A set of 500 candles, sent as a present to a famous temple, were all filled with dynamite. An attempt was also made to assassinate the Foreign Minister by throwing a bomb into his carriage as he was returning from a Cabinet meeting. Neither investigation nor punishment followed, as the intending assassin escaped by the *hari-kari*.

Several explosion outrages have occurred in Spain, Italy, Switzerland, Russia, and the United States. At Seattle, in the latter country, one Schaeffer killed four persons with dynamite and dangerously wounded a fifth. He was at once lynched.

There is a very full account of the Antwerp explosion and fire on September 6. The deaths are said to have been 95, whilst 130 persons were wounded more or less severely. The owner of the establishment, one Corvilain, seems by no means to have adhered to the conditions imposed in his license. He incurred only five-and-a-half years imprisonment and a penalty of £430 as damages!

Certain New Double Iodides of Bismuth and Potassium.—Ch. Astré.—The author has isolated the following compounds:— $(\text{BiI}_3)_2 \cdot 4\text{KI}$; $(\text{BiI}_3)_2 \cdot 3\text{KI} + 2\text{H}_2\text{O}$; $(\text{BiI}_3)_2 \cdot 6\text{KI}$. The number of the known double bismuth and potassium iodides is thus raised to five. They may be considered as resulting from the union of 2 mols. of bismuth iodide with a number of mols. of potassium iodide varying from 1 to 6.—*Comptes Rendus*, vol. cx., No. 22.

On Benzoyl-tannin.—Dr. Carl Böttinger.—This compound was obtained by mixing a cold dilute watery solution of 3 grms. tannin with 5 c.c. strong soda-lye and shaking it up with benzoyl chloride. The substance, after purification, is a crystalline granular powder, insoluble in water, alcohol, and ammonia, but soluble in hot aniline, dimethylaniline, and phenylhydrazine.—*Justus Liebig's Annalen der Chemie*, ccliv., Part 3.

Volumetric Determination of Tannin in Wines.—MM. Roos, Cusson, and Giraud.—The authors prepare a 10 per cent solution of tartaric acid, which is saturated with ammonia until slightly acid. A solution of neutral lead acetate is then added until the precipitate no longer re-dissolves in the liquid, and the whole is filtered. This liquor completely precipitates tannin from its solutions. It is standardised by means of a solution of pure tannin in ether, proceeding as follows:—25 c.c. of the solution of tannin at 5 grms. per litre, i.e., 0.10 of tannin, are placed in a glass with the addition of 4–5 drops of ammonia. The solution of lead aceto-tartrate is dropped in from a burette, at first by 2 c.c. at a time. At the addition of each fresh quantity a drop is taken up with a glass rod and placed upon a double piece of Swedish filter-paper. The precipitate adhering to the rod remains upon the paper at the point touched, whilst the liquid spreads by capillarity and reaches the lower leaf. Near this spot he deposits a drop of a solution of sodium sulphide, taking care that the reagent mixes with the liquid of the first drop by capillarity without touching the precipitate. This precipitate (lead tannate) forms on the paper a spot with distinct outlines, which is darkened by the sodium sulphide, but which does not become surrounded with a brown halo until the moment when all the tannin is precipitated. The first rapid trial gives an approximation of about 2 c.c.; a second trial, made by adding 5 drops at a time, enables the standard to be fixed definitely. Samples of wine are then treated in the same manner.—*Journal de Pharmacie et de Chimie*, xxi., No. 2.

CORRESPONDENCE.

SULPHATES IN NITRIC ACID.

To the Editor of the Chemical News.

SIR,—I do not think there is much ground for Mr. Huxley's perplexity concerning the presence of sulphates in "pure" nitric acid. If he were accustomed to examine all the specimens supplied him he would be in no way surprised at any impurity. Out of five London firms with whom I have dealt for chemicals, one, and one only, has proved even moderately satisfactory in the quality of their "pure nitric acid," and them I caught tripping recently, and it was only after rejecting several samples that I got one reasonably clean, though even then it compared unfavourably with some re-distilled from the ordinary commercial acid in this laboratory without any special precaution whatever.

I believe the cause for this singular state of things lies in the fact that the manufacturer tries to produce a colourless acid at the sacrifice of purity. As to the contamination arising from sodium sulphate in the Winchester quarts, as alleged by the makers supplying Mr. Huxley, if it were not absurd on *a priori* grounds, would be disproved by Mr. Huxley's own experiment.

If every chemist instead of accepting whatever a manufacturer chooses to send him with the magic label "re-distilled puriss." were to regularly examine it, and resolutely and repeatedly send it back, some improvement might result. Moreover, manufacturers should be made aware that their liability for any loss in practice or reputation due to the use of impure chemicals labelled pure, by a chemist confiding enough to rely on that warranty, may be unpleasantly brought home to them through the medium of a court of law.—I am, &c.,

BERTRAM BLOUNT.

Laboratory,
Broadway, Westminster, S.W.
June 14, 1890.

MEDICAL OFFICERS OF HEALTH AND PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—The above subject, on which Mr. Rowland Williams writes (*CHEM. NEWS*, vol. lxi., p. 277), is one of much interest to Public Analysts and still more so to the public, whose interests are greatly in their hands.

I quite agree with the writer, that where the Medical Officer of Health is not well versed in practical chemistry he ought not to hold the double office, but this is no argument when he is competent and where the duties of Medical Officer of Health are insufficient to occupy his whole time. It could not, for example, be contended that the interests of the City of London suffered by the late Dr. Letheby performing the double function, or by Dr. Stevenson or Dr. Tidy holding similar dual offices.

The actual President of the Society of Public Analysts, who is a Medical Officer of Health as well as a Public Analyst, is a decisive proof that the two duties may be associated without disadvantage.

In Birmingham we have a well-known instance of the same kind, and another in the county of Warwick. In none of these instances has any question of incompetency or inefficiency arisen, although in the City of Birmingham alone about 1000 analyses of food, drink, and drugs are made every year.

But it is undeniable that where the Medical Officer of Health is required to perform analytical duties for which he is unqualified there is a great absurdity, and gross injustice is perpetrated, resulting either in little or nothing being done, or a breakdown painfully damaging to the "incompetent analyst." Besides this the work of the Public Analyst is brought into contempt, the place of the

trained analyst is usurped, and great hardship is inflicted on both traders and the public.

It is pointed out that membership of the Institute of Chemistry should be an "indispensable qualification" for a Public Analyst, and I quite agree with the suggestion, as it would be the best guarantee of efficiency.

Mr. Williams refers to a large town in Lancashire where the Town Council a short time since met for the purpose of selecting a Medical Officer of Health and Public Analyst. I do not know what town is indicated, but a friend of mine was quite recently a candidate for the double office also in a large town in the same county, and, although in addition to his holding as high medical and public health qualifications as it is possible to obtain, he is a sound practical chemist of unusually large experience in the special work required, a medallist in both practical and theoretical chemistry, and holds the "indispensable qualification" of membership of the Institute of Chemistry, his special fitness was ignored, and he was unsuccessful in his application for the appointment.

Can it be that the Town Council Committees are incompetent to make a proper choice of a candidate, or is it that "kissing goes by favour?"—I am, &c.,

JOHN WHITE, A.I.C.

Dudley Road, Birmingham,
June 10, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 22, June 2, 1890.

Reduction of Alkaline Sulphates by Hydrogen and Carbon.—M. Berthelot.—It is well known that at about a red heat hydrogen reduces the alkaline sulphates, forming a sulphide and water. This is not an accurate account of the reaction, as there is always formed, along with the water, hydrogen sulphide, and the final product contains caustic alkali. There is produced at the outset a hydrosulphate of the sulphide and an alkaline hydrate; the fixed product formed containing hydrogen, which is commonly supposed to be absent. This primitive reaction is exothermic, 2.6 cal. being set free in case of potassium and 9.3 in the case of sodium. Carbon does not seem to exert a direct action in the industrial reduction of the sulphates which seems to be effected by carbon monoxide. In the present conditions of the manufacture of alkali the reduction of sodium sulphate is a consequence of the two fundamental reactions of hydrogen and carbon monoxide, especially when it is effected in revolver furnaces under the influence of the flame from gases rich in hydrogen, hydrocarbons, and carbon monoxide.

The Determination of the Molecular Weight at the Critical Point.—Philippe A. Guye.—The author lays down the proposition that the critical coefficient of a mixture formed of several different mols. is very approximately equal to the mean critical coefficient of the molecular mixture.

Chloro-Salts of Iridium and its Atomic Weight.—A. Joly.—The physical properties of iridium, as prepared in a state of purity by Mr. Matthey upon the principles ascertained by Sainte-Claire Deville and Debray differ from those formerly supposed. Its sp. gr. is found to be not 21.5, but 22.38. The atomic weight, calculated from the mean result of the author's experiments, is Ir = 192.75, which differs little from the mean found by M. Seubert, Ir = 192.744.

Manganese Oxides obtained in the Moist Way. Manganous Acid.—A. Gorgeu.—Not suitable for useful abstraction.

Soda Alum.—E. Augé.—The author shows that, contrary to the statements of the text-books, soda alum is very slightly efflorescent, and may be kept for months unchanged. Its solubility in water at 16° is only 51 per cent instead of 110 per cent. A solution of soda alum may be boiled indefinitely without ever losing the power of crystallising. In order to obtain soda alum it is merely necessary to concentrate the solution of the aluminium and sodium sulphates to 39°—43° Baumé, to place the paste obtained on plates of lead in an inclined position to collect the mother liquors which make up a fourth of the weight of the amorphous matter, and which carry off nearly all the impurities; crystallisation at the temperature of about 15°; drainage of the crystals.

The Bouquet of Fermented Beverages.—G. Jacquemin.—By adding the special ferments obtained from the wines of Ay, Beaune, Chablis, and Barsac, M. Jacquemin has obtained fermented liquors having the special bouquet of the wines in question from malt and from pure solutions. He has also, by a similar process, produced cider from barley.

MEETINGS FOR THE WEEK.

WEDNESDAY, 25th.—Society of Arts, 4. (Anniversary).

THURSDAY, 26th.—Royal Society Club, 6.30. (Anniversary).

FRIDAY, 27th.—Quekett Club, 8.

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THE CHEMICAL NEWS.

VOL. LXI. No. 1596.

ON THE ANALYSIS OF CERTAIN SAMPLES OF TINNED MEAT.

By C. J. H. WARDEN, M.D., Chemical Examiner to Government;
and Assistant Surgeon C. L. BOSE, M.B.,
Assistant Chemical Examiner to Government.

(Concluded from p. 292).

In order to test the accuracy of alkali determinations made in this indirect manner, the following control experiments were performed:—A solution of pure potassium nitrate and sodium chloride was prepared containing 1.1366 grms. KNO_3 and 0.5326 grm. NaCl in 100 c.c. of distilled water. Of this solution we took 10 c.c. for analysis, and duplicate determinations were made by each of us with the following results:—

Standard solution containing, per cent,			
KNO_3 .	K_2O .	NaCl .	Na_2O .
1.1366	0.529	0.5326	0.273
1.1366	0.529	0.5326	0.273
1.1366	0.529	0.5326	0.273
1.1366	0.529	0.5326	0.273

Found by analysis, per cent,			
KNO_3 .	K_2O .	NaCl .	Na_2O .
1.237	0.577	0.4783	0.2557
—	—	0.4478	0.2373
1.260	0.590	0.430	0.228
1.250	0.586	0.427	0.225

The mean of these experiments shows the error of the process to be as follows:—

	Theory.	Found.	Error.
KNO_3	1.1366	1.2490	+0.1124 per cent.
K_2O	0.529	0.5843	+0.0553 "
NaCl	0.5326	0.4457	-0.0869 "
Na_2O	0.2730	0.2365	-0.0365 "

In the ordinary indirect estimation of the alkali metals, whether as chlorides or sulphates, or by Rose's method, in which the sodium-platinum chloride is decomposed and the sodium chloride extracted by water, gravimetric estimations are generally made, which is hardly necessary to indicate that when only very small amounts of salts have to be estimated, that greater accuracy is likely to result from volumetric than gravimetric methods of estimation. The method we have described appears to yield fairly accurate results, and is specially applicable to cases in which small amounts of sodium and potassium have to be estimated.

For the estimation of chlorine and phosphoric acid about 20 grms. of the fresh pulped meat were carefully weighed in a platinum dish and mixed with about 2 grms. of pure sodium carbonate,* dissolved in sufficient water to cover the pulp. The resulting magma was evaporated to dryness, carbonised below redness, and the residue first extracted with water and then with nitric acid, the solution being passed through a filter. The residue on the filter was dried and added to any particles remaining in the dish. The carbonaceous residue was then ignited until the whole of the carbon was consumed, the ash was again treated with dilute nitric acid, the solution being passed through the same filter; the filtrate and washings being collected in a 250 c.c. flask. The resulting solution was turbid from precipitation of phosphate of lime, the amount of nitric acid and ash being sufficient to neutralise the carbonate of soda. The alkaline solution was consequently rendered faintly acid by acetic acid, and diluted up to 250 c.c. A portion of this solution was

used for the estimation of chlorine. The greater part was concentrated and the phosphoric acid precipitated with molybdenum, but partially weighed as the phosphate of magnesium.

In the dried pulps, nitrogen was determined by Kjeldahl's method, and the results calculated back into the moist meat. The albumenoids were calculated from the nitrogen by using the factor 6.25.

The boiling water extractive was determined by boiling one grm. of the dry pulp with distilled water in a 100 c.c. flask, and, when cold, diluting up to 100 c.c. The liquid was then passed through a dry filter, and a portion of the very faintly opalescent filtrate evaporated to dryness in a platinum capsule for dissolved solids. The greater part of the filtrate was measured into an Erlenmeyer's flask, which was placed in boiling water until the water was evaporated off, and the extractive left as a varnish at the bottom of the flask. Sulphuric acid was then added to the dry residue in the flask for estimation of the nitrogen by Kjeldahl's method.

Fat was determined by very carefully weighing 0.5 to 0.6 of a grm. of the dry pulp into a small accurately stoppered weighing bottle, and adding a measured volume of light petroleum ether from a burette. The mixture was allowed to digest with agitation for about two days, then allowed to clear by subsidence, and a portion of the

perfectly clean supernatant liquid withdrawn by a small burette, and a carefully measured volume discharged into a tared beaker. After evaporating off the ether, the residual fat was heated to 100° C. and weighed. No correction was applied for increase in volume of the petroleum spirit due to dissolved fat. This method is one suggested by Dragendorff,* for the estimation of oil, in his scheme for the systematic analysis of vegetable substances by the aid of various solvents. As a control experiment, one of us estimated the fat in a sample in the manner described, while the other determined it by thoroughly exhausting a portion with petroleum ether with the following results:—

a. By Dragendorff's method, fat = 15.016 per cent.

b. By thorough exhaustion, fat = 15.030 "

Working in the manner indicated the general results of the determination of the samples are shown in next page.

In order to compare the composition of tinned with fresh meat, the following analyses by König† of fresh meat are appended.

Nature of samples.	Water.	Albumenoids.	Fat.	Ash
Very fat ox flesh, mean of 7 analyses	55.42	17.19	26.38	1.08
Moderately fat ox flesh, mean of 21 analyses:				
Minimum	68.50	16.23	1.17	0.71
Maximum	78.00	25.35	9.50	1.95
Mean	73.25	20.78	5.33	1.33
Lean ox flesh, mean of 9 analyses	76.71	20.78	1.50	1.18
Fat cow flesh, mean of 9 analyses	70.96	19.86	7.70	1.07
Lean cow flesh, mean of 6 analyses	76.35	20.54	1.78	1.32
Very fat mutton, mean of 3 analyses	47.91	14.80	36.39	0.85
Moderately fat mutton, mean of 8 analyses ..	75.99	17.11	5.77	1.33

* "Plant Analysis."

† Zusammensetzung der menschlichen Nahrungs- und Genussmittel.

* The addition of sodium carbonate is recommended by Dr. Stutzer to prevent the formation of pyrophosphoric acid and the volatilisation of small quantities of chlorine during ignition.

Description of brand.	Percentage.													
	Moisture at 120° C.	Fat.	Nitrogen.	Albumenoids N × 6.25.	Total ash.	Ash soluble in water.	Ash insoluble in water.	Chlorine (Cl).	Phosphoric anhydride (P ₂ O ₅).	Oxide of potassium (K ₂ O).	Oxide of sodium (Na ₂ O).	Boiling water extractive per cent on meat.	Nitrogen in boiling water extractive, per cent on meat.	Meat bases and in boiling water extract = N × 6.25.
Sydney Meat Preserving Co. Mutton..	54.700	15.030	4.40	27.500	1.5302	1.3039	0.2263	0.544	0.345	0.364	0.417	7.249	0.906	5.660
New Zealand Packing Co. Beef ..	57.350	10.338	4.05	29.062	0.991	0.605	0.336	0.146	0.339	0.220	0.117	6.953	1.000	6.250
" Mutton ..	55.000	14.000	4.30	26.275	0.621	0.189	0.432	0.112	0.304	0.136	0.067	5.353	0.900	5.625
Faibank Canning Co. Beef ..	56.039	15.829	3.93	24.562	1.944	1.778	0.165	1.107	0.308	0.262	0.807	7.159	0.879	5.493
Armour Packing Co. Beef ..	50.650	18.660	3.99	24.937	4.365	4.716	0.189	2.650	0.338	0.434	0.963	10.414	0.987	6.168
Central Queensland Meat Export Co. Beef ..	49.050	22.080	4.20	26.25	1.716	1.474	0.242	0.999	0.402	0.230	0.609	7.951	1.010	6.312
" Mutton..	52.600	14.390	4.51	28.187	1.605	1.244	0.361	0.847	0.349	0.237	0.458	9.464	1.100	6.875

Description of samples.	Water.	Albumenoids	Fat.	Ash.	In anhydrous samples.		Albumenoids in anhydrous and fat-free sample.
					Nitrogen.	Fat.	
Wilson Export Co.	57.3	28.9	10.2	3.6	10.83	23.75	88.75
(?) Canning and Co. Export Co.	49.2	25.7	21.6	3.5	8.09	42.52	87.93
Brougham Export Co.	48.9	27.7	19.0	4.4	8.67	37.18	86.25
From Australia	54.03	29.31	12.11	4.55	10.20	26.34	86.50
Pressed corned beef, from Chicago	56.9	33.8	6.4	2.9	12.55	14.85	91.06
2-lb. tin containing 1020 grms.	57.7	31.5	7.3	3.5	11.91	17.62	92.81
4-lb. tin containing 1844 grms.	58.8	25.9	11.8	3.5	10.05	28.64	87.12
Mean	54.69	28.97	12.63	3.71	10.33	27.27	88.63

Calculating the albumenoids on the anhydrous and fat-free meat gives 90.34 as the percentage, figures which are also higher than the albumenoid content of the tinned meats. According to Playfair's experiments, it would appear that in roasting meat the loss is chiefly water, the proportion of carbon, hydrogen, nitrogen, and oxygen remaining the same.*

Summarising we may state that our results generally confirm those of other analysts, as indicating the lower nutritive value of tinned when compared with fresh meat. Our inferences are based on purely chemical data, but on physiological grounds there can also be no doubt that sodden tinned meat would be less easily assimilated than ordinarily cooked flesh, and that consequently its dietetic value would be even less than is indicated by its chemical composition.

THE SEPARATION AND DETECTION OF Al, Cr, Fe, Co, Ni, Zn, Mn, Ba, Sr, Ca, Mg, K, Na, NH₄†

By J. S. C. WELLS, Ph.D.
(Concluded from p. 299).

Metals of First and Second Groups.

17. To a small portion of the solution in which ammonia and ammonium sulphide have failed to produce a precipitate, or of the fluid filtered from such precipitate, add NH₄Cl (if not already present), NH₄OH, and (NH₄)₂CO₃, and heat gently for a few minutes (Note 20).

18. No precipitate forms.

Absence of Ba, Sr, and Ca, at least in notable quantity (Note 21). Traces, however, may be present; to detect them, proceed as follows:—Add to a portion of the solution some (NH₄)₂SO₄; if the fluid becomes turbid it contains traces of barium.

To another portion add some (NH₄)₂C₂O₄, and allow to stand a few minutes; if a precipitate forms, traces of calcium are present.

Treat the remainder of the solution, a portion of which you have just tested, according to 24.

19. A precipitate is formed.

Presence of Ba, Sr, and Ca. Treat the whole filtrate with NH₄OH and (NH₄)₂CO₃; heat gently for some time and filter; take two portions of the filtrate and test one with (NH₄)₂SO₄ for traces of barium, the other with (NH₄)₂C₂O₄ for traces of calcium, which may possibly be present; if found, mix the two solutions and filter, and test the filtrate for magnesium according to 24. The remainder of the filtrate, to which neither (NH₄)₂SO₄ nor (NH₄)₂C₂O₄ has been added, is tested for potassium and sodium according to 25 or 28, the method used depending on whether magnesium is present or not.

20. Precipitate produced by (NH₄)₂CO₃ (contains BaCO₃, SrCO₃, CaCO₃).

Dissolve in least possible quantity of HCl, H₂O₂. Take a small portion of this solution and add to it some CaSO₄.

The course of proceeding now depends on whether the CaSO₄ gives an immediate precipitate or not.

21. CaSO₄ causes an immediate precipitate—proves Ba. To the remainder of the acetic acid solution add a slight excess (Note 22) of K₂Cr₂O₇, and filter. Precipitate contains BaCrO₄ (yellow). To the filtrate add NH₄OH to alkaline reaction, and then (NH₄)₂CO₃; heat gently and filter. Reject filtrate. Dissolve the precipitate, consisting of SrCO₃ and CaCO₃, in acetic acid, divide solution into two parts, a and b.

22. a. Add an excess of CaSO₄, heat gently and shake well. A white precipitate proves Sr. (In dilute solutions the precipitate forms very slowly).

b. If strontium has been found in "a" (Note 23), add an excess of (NH₄)₂SO₄ to solution "b," boil, keeping solution alkaline with NH₄OH, and filter. Reject precipitate (Note 24).

To the filtrate add (NH₄)₂C₂O₄—a white precipitate shows presence of Ca.

If Sr is not present, the addition of the (NH₄)₂SO₄ is omitted, and the calcium tested for directly with NH₄OH and (NH₄)₂C₂O₄.

23. CaSO₄ does not give an immediate precipitate.

In this case add a little more of the acetic acid solution to it, and test for strontium according to 22, a. Then take balance of solution and treat it for calcium as directed in 22, b.

24. FILTRATE FROM (NH₄)₂CO₃ PRECIPITATE, OR SOLUTION IN WHICH THAT REAGENT HAS FAILED TO GIVE ONE.

Contains magnesium and the alkalis. Take the portion of the filtrate that has been freed from traces of Ba and Ca, by means of (NH₄)₂SO₄ and (NH₄)₂C₂O₄ (see 19), and add to it NH₄OH and Na₂HPO₄—a white crystalline precipitate proves the presence of Mg.

The method of testing for Na and K now depends on whether magnesium is present or not.

25. Magnesium is present.

As Mg interferes with the test for the alkalis, it must be removed before testing for them.

Evaporate the balance of the filtrate from the (NH₄)₂CO₃ precipitate (19) to dryness, and ignite until all ammonium salts are expelled. Dissolve the residue in a little water, add baryta-water as long as a precipitate forms, boil, filter; add to filtrate NH₄OH and (NH₄)₂CO₃, heat gently, filter and evaporate filtrate to dryness (add a little NH₄Cl during the evaporation, so that any alkaline hydroxide or carbonate will be converted into chloride) (Note 25); ignite gently until all ammonium salts are volatilised, then dissolve in a very little water, and test for Na and K, according to 26 and 27.

26. Test the concentrated solution in the flame on platinum wire. A strong yellow flame proves sodium. Confirm by adding to a portion of the solution some K₂H₂Sb₂O₇ (freshly prepared)—a white sandy precipitate indicates sodium. (In dilute solutions the precipitate forms very slowly; its formation is aided by rubbing watch-glass on which test is made with a glass rod).

27. To the remainder of the solution add a few drops of PtCl₄—a yellow crystalline precipitate proves K. If no precipitate forms on addition of PtCl₄, evaporate the solution nearly to dryness and add alcohol; this will show

* Parkes's "Hygiene."

† School of Mines Quarterly, Vol. xi., No. 3.

the presence even of traces of K, by leaving undissolved a yellow powder consisting of K_2PtCl_6 .

28. Magnesium is not present.

In this case it is only necessary to evaporate the solution to dryness, ignite carefully to drive off all ammonium salts, then dissolve residue, if any, in a very little water, filter if necessary, and test for Na and K according to 26 and 27.

29. Ammonia still remains to be tested for. Treat a portion of the original solution with KOH or $Ca(OH)_2$. Test the liberated gas, if any, with moistened red litmus paper; if it turns blue, ammonia is present (colour disappears on drying the test-paper).

Notes.

Note 1.—If the fluid is colourless, it contains no chromium. If coloured, the tint will to some extent act as a guide to the nature of the substance present; thus a green tint or violet tint turning green upon boiling, points to Cr; a light green to Ni; a reddish colour to Co; the turning yellow of the fluid upon boiling with HNO_3 to Fe.

It must be remembered, however, that these tints, except the last, are perceptible only if the metals are present in considerable quantity, and also that complementary colours, such as the green of Ni and the red of Co, will destroy each other, and that such a solution may be colourless.

Note 2.—The H_2S comes from the previous precipitation of the 5th Group metals, by that reagent. If not removed, it would cause a precipitation of sulphides on the addition of NH_4OH , and thus hide the reaction given by the latter.

Note 3.—The FeO should be oxidised to Fe_2O_3 , so that it will be precipitated on the addition of NH_4OH .

Note 4.—This only holds good for Al and Cr in the absence of non-volatile organic substances, especially acids such as citric and tartaric. Citric acid may also prevent the precipitation of Mn.

If organic matter is present, it should be removed by evaporating the whole of the solution used for the 3rd and 4th Groups to dryness and gently igniting.

It is a good plan to moisten the dry residue before igniting with a little HNO_3 (conc.). The ignited residue is then dissolved by boiling with a small quantity of strong HCl and filtering from any insoluble residue. The solution is now ready to be tested in the usual way.

Note 5.—The presence of much NH_4Cl has a great tendency to prevent the precipitation of borates and fluorides of the alkali-earth metals.

Note 6.—Magnesium oxalate is thrown down from HCl solution by NH_4OH only after some time, and never completely: dilute solutions are not precipitated by NH_4OH .

Note 7.—Phosphates, borates, &c., of the alkali-earth metals cannot exist in a neutral solution.

Note 8.— NH_4Cl is added to prevent the precipitation of magnesium and manganese; it also promotes the precipitation of the metals of the 4th Group as sulphides.

Note 9.—A large excess of NH_4OH should be avoided, as it increases the solubility of NiS in $(NH_4)_2S$, and dissolves some $Al_2(OH)_6$.

Note 10.—If the filtrate is dark brown, it indicates the presence of nickel, since NiS, under certain conditions, is slightly soluble in ammonium sulphide, especially if the latter contains any polysulphides (indicated by colour of the solution). Boil until $(NH_4)_2S$ is all decomposed and the free ammonia driven off, then add a few drops of dilute HCl, and filter from the precipitate of NiS and S. Make filtrate alkaline with NH_4OH , and proceed according to 17.

Note 11.—The addition of a little $(NH_4)_2S$ to the wash water prevents the oxidation of the sulphides to sulphates, a reaction likely to occur when they are exposed to the air.

Note 12.—Observe colour of precipitate—if pure white it indicates absence of iron, cobalt, and nickel.

Note 13.—Iron is tested for in the original solution with $K_3Fe(CN)_6$, and NH_4CyS in order to determine which oxide is present, since after treatment with H_2S or $(NH_4)_2S$ it is always in the form of a ferrous salt, owing to the reducing action of these reagents. When making the test with NH_4CyS , if the colour does not appear on the addition of this reagent, add an excess of HCl to the test; this will counteract the influence of phosphates, borates, &c., which interfere when present.

Note 14.—Iron must always be in the ferric form for precipitation by $NaC_2H_3O_2$ or $BaCO_3$.

If the iron is not completely oxidised, there is likely to form a red modification of ferric oxide that runs through the filter paper and is very insoluble.

Note 15.—If the colour of the solution indicates manganese, heat it with a few drops of alcohol, and filter from the precipitated oxide of manganese.

Note 16.—The $KClO_3$ is added to the fusion mixture to oxidise any chromium that might possibly have been left unacted on by the bromine, and then precipitated with the basic acetates.

Note 17.—Be careful not to mistake a slight precipitate of sulphur, which is quite likely to form in the hot acid solution, for one of ZnS. In case of doubt, confirm by the blowpipe test with $Co(NO_3)_2$. A very delicate way of making this test is to dissolve the supposed ZnS in a few drops of HCl, then add a drop or two of $Co(NO_3)_2$; precipitate mixture with Na_2CO_3 , boil, filter and wash, and ignite precipitate on platinum foil. On triturating the residue the green colour will be distinctly seen.

Note 18.—Instead of the separation given in 12, the following method may be used:—

To the filtrate from the $BaCO_3$ precipitate add H_2SO_4 (dilute) in sufficient quantity to precipitate all of the barium in the solution, heat to boiling, and filter.

To the filtrate add KOH in excess; the manganese precipitates as $Mn(OH)_2$ (turning brown on exposure to the air), filter and pass H_2S into the filtrate—a white precipitate proves Zn. The precipitate is sometimes dark coloured, owing to impurities; in doubtful cases always test it by the blowpipe. (See Note 17).

Note 19.—The precipitate is dissolved in HCl, and then precipitated with NH_4OH , in order to get rid of the excess of $BaCO_3$. In cases where there is only a slight excess of $BaCO_3$, this operation may be omitted.

Note 20.— NH_4OH is added to prevent the possible formation of any bicarbonate, and also because the precipitate of the carbonates is more insoluble in ammonia water than in pure water. Heating causes the amorphous precipitate to contract and become crystalline, in which condition it is much more readily filtered; also decomposes any bicarbonate.

Note 21.—Owing to the slight solubility of $BaCO_3$ and $CaCO_3$ in NH_4Cl , traces of these metals are often held in solution by the NH_4Cl present in the solution.

Note 22.—A large excess of $K_2Cr_2O_7$ is to be avoided, especially in presence of much acetic acid, since $BaCrO_4$ is slightly soluble in chromic acid. The filtrate should only be coloured a pale yellow by the excess of $K_2Cr_2O_7$ contained in it.

Note 23.—It is not necessary to wait to see if Sr is found in "a" before testing for Ca. Proceed just in the same manner as if Sr was present, adding $(NH_4)_2SO_4$, boiling and filtering, and testing filtrate with the oxalate for calcium.

Note 24.— $(NH_4)_2SO_4$ precipitates calcium from strong solutions, so that the formation of a precipitate on the addition of this reagent does not prove the presence of Sr, unless the precipitate is repeatedly boiled with the $(NH_4)_2SO_4$ and NH_4OH , which will finally remove all of the $CaSO_4$, leaving only the $SiSO_4$.

Note 25.—In cases where the alkalies are present in the original solution as sulphates, the addition of $Ba(OH)_2$ to remove the magnesium converts them into hydroxides, and the latter, on the addition of $(NH_4)_2CO_3$ to precipitate the barium, are changed to carbonates.

THE SEPARATION AND DETERMINATION OF ZINC IN PRESENCE OF IRON AND MANGANESE.

By J. RIBAN.

THE methods hitherto proposed for the difficult determination of zinc in presence of iron generally require the previous separation of the iron in a form which renders it unfit for direct weighing, and besides the metal carries down with it valuable proportions of zinc. Hence it is necessary to re-dissolve and re-precipitate it before proceeding to the ultimate determination of the zinc. We are thus led to the successive washing of two gelatinous precipitates of iron, an operation always long and troublesome if this metal is in notable quantity. Further, in the analysis of a great number of ferruginous zinc ores it may be desirable to determine this latter metal first, or even exclusively; the iron, manganese, &c., having but a secondary importance or none at all. Some methods used for the initial determination of zinc do not allow of its determination in presence of lime, which occurs in the gangue of certain ores.

The author proposes a process which gets rid of all these difficulties and permits of the direct gravimetric determination of zinc. It is founded on the following facts established in a former memoir (*Comptes Rendus*, cvii., p. 341). (1) Zinc, in presence of alkaline or ammoniacal hyposulphates, gives with sulphuretted hydrogen a precipitate of sulphide, dense, granular, easy to wash, and insoluble in the cold by hyposulphuric acid set free; (2), iron is not thrown down by sulphuretted hydrogen in presence of the hyposulphates, and zinc, if present, carries down mere traces of iron.

For the direct determination of zinc in presence of iron (ferric or ferrous) and manganese the solution is first brought to such a degree of dilution that it contains at most 0.1 grm. zinc in 100 c.c.; it is then saturated with a solution of sodium carbonate until there appears a slight permanent precipitate, which is re-dissolved in a few drops of dilute hydrochloric acid. A current of sulphuretted hydrogen is then passed into the cold liquid, when the greater part of the zinc is precipitated with sulphur, derived from the reduction of the ferric salt; a large excess of a solution of sodium hyposulphate is then added, and the current of sulphuretted hydrogen is continued. The last remains of the zinc are precipitated, but the iron remains in solution. An excess of hyposulphate is not injurious. For these determinations it is convenient to prepare a solution of known strength and to pour in double the theoretical quantity as approximately calculated for the double decomposition with the zinc and iron. The use of an excess of hyposulphate supersedes the precautions.

If after the precipitation of the zinc it is proposed to determine the iron by means of ammonia, as ferric oxide always carries down some proportion of alkaline salts, it is preferable to use ammonium hyposulphate, which is now also an article of commerce. The initial saturation of the free acid in the solutions is effected, not with sodium carbonate, but with ammonia or ammonium carbonate, until the yellow colouration of the solution containing iron passes to orange, the colour of the neutral or basic salts of this metal.

The precipitate of zinc sulphide, which is dense and collects readily, is white, sometimes greyish from the presence of traces of iron, which may be easily or quickly determined, as it will be seen. The precipitate is let stand for five or six hours at least, and is washed by decantation and filtration in hot water to which a solution of sulphuretted hydrogen has been added, when it very often takes a slightly violet tint; the washing is completed on the filter. The precipitate is ignited with sulphur in a current of hydrogen (H. Rose's apparatus) and weighed; it consists of zinc sulphide containing very small quantities of iron sulphide, which render it slightly

greyish. These traces are determined by dissolving the contents of the crucible in hydrochloric acid, peroxidising with a few drops of nitric acid, and then supersaturating with ammonia after the addition of a large excess of ammonium chloride to prevent the precipitation of the zinc. The quantity of iron carried down by the zinc is so slight that ammonia produces no precipitate in the cold, and it must be raised to a boil to cause a few light flocks of ferric hydroxide to appear. They are collected on a small filter and washed with solution of ammonium chloride. The weight of this peroxide is re-calculated into iron sulphide, which is deducted from the weight of the zinc sulphide as previously found, thus giving the nett weight of the latter.

If we wish to determine the iron in the liquids freed from zinc, it is sufficient to concentrate them and peroxidise with nitric acid, which throws its action immediately upon the iron, the hyposulphates being scarcely attacked. From the solution the iron is thrown down with ammonia in the ordinary manner.

The same method admits of the exact separation of zinc from manganese; zinc sulphide carries down merely inponderable quantities of manganese.

This method has been applied successfully to the analysis of ferruginous calamines; if they are at the same time plumbiferous it is necessary, first, to eliminate the lead, which would otherwise be precipitated along with the zinc by the sulphuretted hydrogen.—*Comptes Rendus* (cx., p. 1196).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolitan Water Act, 1871.

London, June 7th, 1890.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, all were found to be clear, bright, and well filtered, excepting two, one of which was recorded as "slightly turbid," and one as "very slightly turbid."

The variations in mean composition of the water supplied to London, noticeable from month to month, continue to be, as is usually the case, confined within so limited a range as to afford very little occasion for remark or comparison. During the past month the maximum proportion of organic carbon present in any single sample of Thames-derived water examined was found to be 0.173

part in 100,000 parts of the water, corresponding to about only three-tenths of a grain of organic matter per gallon. The mean proportion of organic carbon present in the May supply was found to be 0.156 part in 100,000 parts of the water, as against a mean of 0.148 part in the April and of 0.154 part in the March supply.

We are, Sir,
Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 5th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MESSRS. W. B. Shuttlewood and H. R. Kenwood were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Charles Edwin Day, 1, Merchiston Bank Terrace, Edinburgh; Robert Frost, St. James's Chambers, Duke Street, S.W.; George German, Huntingdon House, Ashby de la Zouch; Colin Gordon, Millwall Club, West Ferry Road, Millwall, E.; Frank Haydon, Ettrick, Putney Common, S.W.; Arthur E. Palmer, Ashley Mount, Tettenhall, Wolverhampton; Thomas Parkes, Grammar School, Stamford; Edward Cox Seaton, 35, George Street, Hanover Square, W.; James Mitchell Wilson, Hall Gate, Doncaster.

The following papers were read:—

45. "*The Production of Pure Metallic Copper in a Crystalline Condition.*" By C. C. DUNCAN, King's College, London.

The method of precipitating copper oxide from a boiling solution of copper sulphate with potassium hydroxide and then reducing in electrolytic hydrogen having been found unsatisfactory, as the last traces of sulphate could not be washed away, experiments were made on the reduction of the sulphate by zinc.

To a solution containing several grms. of purified sulphate made acid with chlorhydric acid, metallic zinc (containing only a trace of lead) was added in small fragments. Dark spongy-looking copper at once separated, and this soon protected the zinc from the action of the acid; consequently the copper was very slowly deposited: it was found to be in the form of feathery dendritic crystals.

A portion of the crystalline copper, well washed with dilute chlorhydric acid and distilled water, was dissolved in strong nitric acid free from sulphuric, the solution was diluted, and barium nitrate added; no precipitate of any kind formed, even after standing forty-eight hours, showing the absence of sulphur.

To discover whether the metallic copper contained zinc, two of the finest crystals (about 8 m.m. long) were again well washed and dried in hydrogen. These crystals were then fixed in an ordinary spark-stand, and the spark from a 2-inch Appa's coil, with a Leyden jar of one quart capacity in the circuit, was passed between them. The light from the copper terminals was analysed by one of Browning's two-prism spectroscopes, and the spectrum given by the copper was compared with that of zinc. None of the lines of zinc coincided with those given by the copper; it was therefore assumed that zinc was absent.

The bright lines given by the copper crystals agreed with those described by Thalèn ("*Mémoire sur la détermination des longueurs d'onde des raies métalliques.*" *Act. Nova Upsal.*, iii., vi., 1868, 29).

The spark and lines were extremely bright and no faint lines were to be seen (except the usual air-lines), showing the absence of any metallic impurity.

Microscopic examination proved the dendritic crystals to be built up of octahedrons. As the production of these crystals was quite accidental, experiments were made with different strengths of copper sulphate solutions, with and without free acid, in order to reproduce them.

In the literature relating to the reduction of metallic copper from its salts by means of metallic zinc, there is no mention whether the copper so reduced is in the crystalline state, except in a paper by Dr. Gladstone and Mr. Tribe (*Proc. Roy. Soc.*, xx., 1872, 219), who mention the deposition of metallic copper in a crystalline condition, but they make no remark on the purity or size of the crystals so formed.

In another paper, "On the Crystallisation of Silver, Gold, and other Metals" (*Proc. Roy. Institute*, vi., 1872, 428), Dr. Gladstone again refers to crystalline copper in the following terms:—

"Copper salts give round nodules which have no crystalline appearance when deposited from moderately weak solutions, but a very strong solution of the chloride—about 40 per cent—yields with zinc first a black thick

	CuSO ₄ .	Water.	Acid.	Results.
I.	10 grms.	400 c.c.	0	Copper was at once reduced in spongy state and then in minute dendritic crystals just visible to the unaided eye. The spongy copper proved to be composed of octahedrons under the microscope. The crystals did not increase in size on standing.
II.	20 grms.	400 c.c.	0	} Same as I.
III.	50 "	400 "	0	
IV.	10 "	400 "	10 c.c.	
				The dendritic crystals produced were larger than any of those in I., II., and III.
V.	20 "	400 "	10 "	} Same as IV.
VI.	10 "	400 "	100 "	
				Crystals of copper which were slightly larger than those produced in V.
VII.	20 "	400 "	200 "	} Dendritic crystals of copper were produced, several of which were 10 m.m. in length. Sulphur was detected in these crystals, and in most other crystals which had been reduced in a solution which was very strongly acid. No zinc was detected by the spectroscope.
VIII.	40 "	400 "	200 "	The crystals produced were only very slightly larger than those in VII., but more numerous.

growth, then arborescent fringes of red metal terminating in crystals of very appreciable size."

In all the experiments made by the author with acid and neutral copper solutions, dendritic crystals of copper were found which could be seen with the unaided eye; they were small in the case of neutral, and large in the case of acid solutions.

The accompanying tables give the quantity of copper sulphate, water, and chlorhydric acid (relative density 1.152) used in the different experiments, and the results.

As sulphur had been detected in several of the crystals deposited from the copper sulphate solutions, a few experiments were made with copper chloride free from sulphate.

	CuCl ₂ .	Water.	Acid.	Results.
I.	10 grms.	400 c.c.	0	Small dendritic crystals of copper were quickly produced. On standing, the crystals increased slightly in size.
II.	20 "	400 "	0	Numerous small dendritic crystals with several about 7 m.m. long. No impurity detected.
III.	10 "	400 "	20 c.c.	Two or three crystals about 11 m.m. long with the usual mass of smaller crystals. No impurities were detected.
IV.	40 "	400 "	20 "	Four or five crystals 12 m.m. long with the usual mass of smaller crystals. No impurity detected.
V.	140 "	500 "	40 "	This solution gave the finest crop of dendritic crystals yet produced. One crystal measured 15 m.m., and its lateral branches were composed of clumps of crystals. The crystals were erect, and had a beautiful metallic appearance. Several of the crystals were from 5 to 8 m.m. in length, two or three 12 to 13 m.m., and only a little spongy copper was to be seen. No impurity could be detected.

The pure crystalline copper is insoluble in pure nitric acid (free from nitrous acid). See Veley (*Proc. Roy. Soc.*, 1890).

Crystalline copper is said to have been obtained by using iron and aluminium as reducing agents. Thus Gore, in his text-book of "Electro-Metallurgy," pp. 203-204, refers to the use of iron in recovering copper from large deposits of the Tharsis and Rio Tinto mines in Spain. The copper is dissolved by means of chlorhydric acid, and the liquid is run into large vats filled with scrap

iron. In a short time all the copper is reduced in the form of feathery crystals upon the iron. The process is described by P. Argall and G. A. Kinahan in the *Sci. Proc. Roy. Dublin Soc.*, N.S., iii., 1883, 302-328, and on p. 309 the production of crystalline copper is mentioned. No reference is made to the purity or size of the crystals.

The reduction of copper from its sulphate by the aid of aluminium is mentioned in "Watts' Dictionary of Chemistry," 2nd Sup., 1875, p. 383, in a passage which is extracted from Cossa (*Nuovo Cimento* [2], iii., 75). The crystals of copper are described as follows:—"Aluminium foil immersed in a solution of sulphate or nitrate of copper is not acted upon at once, but after two days the foil becomes covered with crystals consisting partly of dendrites, but for the most part of well-defined octahedrons." It was found that if the solution of the copper sulphate is neutral, only octahedrons are produced; but that if an acid is present, dendrites are produced. Sulphur was the only impurity detected.

"Copper is immediately reduced by aluminium from a solution of cupric chloride, and likewise, though more slowly, from the acetate." It is not mentioned whether the copper is deposited in the crystalline or amorphous state, but the author has found, on experimenting with these substances, that dendritic crystals of copper are produced in both cases. No impurity could be detected.

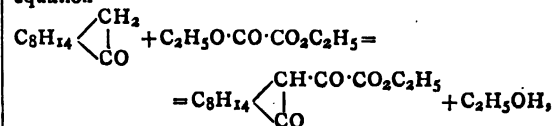
Magnesium was found to reduce copper from a solution of copper sulphate in very small quantities, the copper being formed in small patches composed of dendrites and octahedrons. Magnesium added to a solution of copper chloride caused an evolution of gas, throwing down a green precipitate, and at the same time reducing the copper in the spongy state. The well-washed copper contained magnesium.

In a note by M. A. Commaille "On the Action of Magnesium on Neutral Metallic Salts" in the *CHEMICAL NEWS*, xiv, 188, it is mentioned "that copper sulphate gives with magnesium the metal (copper), the hydrated peroxide and a green subsalt. With the chloride no metal (copper) is precipitated, but a deposit of Brunswick green."

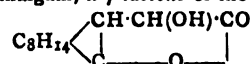
In experiments made by the author with the chloride, copper was reduced in appreciable quantity, but in an entirely amorphous state.

45. "The Action of Ethylic Oxalate on Camphor." By J. BISHOP TINGLE, Ph.D.

The author finds that camphor and ethylic oxalate in presence of metallic sodium interact according to the equation



forming *ethylic camphoroxylate*. This is an oily liquid, which decomposes on distillation; on hydrolysis it is converted into *camphoroxylic acid*, which crystallises in rhombic plates melting 88° C. On reducing this acid with sodium amalgam, a γ -lactone of the formula



is obtained, melting at 75-76°. Ethylic camphoroxylate and phenylhydrazine interact to form a *monophenylhydrazone*, which crystallises in white needles melting at 187-188° C. By the action of hydroxylamine a compound is formed which melts at 193° and will be further investigated. On ethylic camphoroxylate with aniline to 165°, *oxanilide* is produced.

46. "The Oxidation of Turpentine in Sunlight." By HENRY E. ARMSTRONG.

It was pointed out by Sobrero in 1851 (*C. R.*, xxxiii, 66) that when turpentine is exposed to light in presence of

moisture and oxygen a crystalline substance is formed which has the composition represented by the formula $C_{10}H_{18}O_2$; and that this substance is decomposed when boiled with dilute sulphuric acid, an oil being formed which has a powerful odour recalling both that of camphor and that of turpentine. The author's attention became directed to this substance about twelve years ago in the course of his studies of the terpenes and camphor, and in most years since, during the summer, he has carried on experiments on the oxidation of $C_{10}H_{16}$ hydrocarbons in sunlight, and has been able to confirm Sobrero's statements in every particular. As the crystalline product in question has not yet been named, it is proposed to term it—at all events, provisionally and until its constitution is determined—*sobrerol*.

Sobrerol is readily soluble in alcohol, and crystallises from this solvent usually in large, flexible, monosymmetric prisms having a peculiar hour-glass structure inside and showing hemihedrism. It is slightly soluble in water, benzene, chloroform, and petroleum spirit; the aqueous solution has a bitter taste. It melts at about 150° . The results obtained on analysis (carbon, 70.57 and 70.49 per cent; hydrogen, 10.71 and 10.74 per cent) show that, as Sobrero states, it has the formula—



and there can be very little doubt that it is a glycol; but, owing to its extreme sensitiveness, to the action of acids, it is difficult to prove this by the ordinary methods. Sobrerol is optically active in a high degree, the apparent specific rotatory power of the products from French turpentine in a 5 per cent. solution in alcohol (B.P.) being slightly above 150° . Sobrerol from American turpentine (from Savannah) was found to have about the same rotatory power, but in the opposite direction. The optical similarity of the two products is noteworthy, inasmuch as the American has less than half the rotatory power of French turpentine. It would seem that only the terpenes proper, and not the citrenes, &c. (cf. *Chem. Soc. Trans.*, 1879, 734; *J. Soc. Chem. Ind.*, 1882, 478) form sobrerol. To ascertain whether this be the case, and what are the crystallographic and optical relationship of the products obtained from terpenes from different sources, the author is engaged in conjunction with Mr. W. J. Pope—to whom he is indebted for assistance in this research—in studying the behaviour of pure $C_{10}H_{16}$ hydrocarbons of all kinds.

When boiled with dilute sulphuric acid, sobrerol is readily converted into the oil referred to by Sobrero; the product is undoubtedly identical with the isomeride of camphor which Wallach and Otto have obtained by treating turpentine with nitrous acid (*Annalen*, ccliii, 249), and which they have provisionally named *pinol*; as the compound is not an *ol*, i.e., an alcohol, it may be suggested that it might appropriately be termed *sobrerone*. The product from sobrerol begins to boil at 150 – 160° , but passes over almost entirely at about 183° , leaving a small amount of a viscid oil; it readily combines with bromine, forming a dibromide (bromine found 50.78 per cent) which crystallises very beautifully in forms of the rhombic system, the lengths of the axes being in the ratio $a : b : c = 0.5696 : 1 : 1.5553$, dimensions which almost absolutely agree with those quoted by Wallach and Otto, viz., $a : b : c = 0.5700 : 1 : 1.5553$. The dibromide was found to melt at 93.5° , 94° being the melting point given by Wallach and Otto.

The formation of sobrerone from sobrerol is of interest as serving to explain its formation by Wallach and Otto's method: very probably sobrerol is first produced, and is at once acted on by the acid. Sobrerol is probably always the initial product of oxidation of turpentine. It may be expected that sobrerone will be found among the oxygenated constituents of some essential oils, and it is proposed to search for it.

If, as appears probable, sobrerol be a glycol, the formation of sobrerone from it is analogous to that of pinacol from pinacolone; but in this latter case, an isomeric change

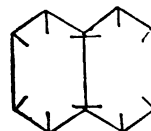
takes place, pinacolone being a ketone, $CM_3 \cdot CO \cdot CH_3$, and not the oxide corresponding to pinacolone. Wallach and Otto's observations, however, show that sobrerone is not a keto-compound. It would, therefore, appear to follow that sobrerone is an oxide formed by withdrawal of the elements of a water molecule from two hydroxyls attached to contiguous carbon atoms.

47. "The Structure of Cycloid Hydrocarbons." By HENRY E. ARMSTRONG.

The appearance of Bamberger's remarkable paper (*Annalen*, cclvii, 1; *Ber.*, 1890, 1124), in which formulae are proposed for naphthalene, anthracene, &c., apparently analogous to that suggested by v. Baeyer and the author for benzene, renders it desirable that the cases in which this formula is applicable should be carefully considered, especially as the somewhat novel conceptions which the author would associate with this symbol tend to limit the extension of the hypothesis.

Although superior to all other symbolic expressions in almost every respect, Kekulé's formula is, nevertheless, admittedly open to the objections (1) that it apparently involves the existence of two ortho- and two meta-derivatives; and (2) that it represents benzene as containing three pairs of carbon-atoms in the condition of those in ethylene. The *centric* formula was developed to meet these objections. It represents benzene as a symmetrical configuration, and is suggestive of only three derivatives. The six affinities which in Kekulé's symbol act in pairs, as in ethylene, are assumed actually to neutralise each other much as the affinities do in paraffins, but without constituting cross linkages within the ring as represented in the Claus formula, for example: the behaviour of the hydrotrepthalic acids, of quinone and of anthracene, and among others, Kekulé's researches on the constitution of pyridine, of which he recently gave an account in Berlin, affording, in the author's opinion, abundant evidence of the non-existence of such cross linkages. The conception in his mind, to which, however, expression has not hitherto been given, has always been that the centric affinities act within a cycle rather than merely towards the centre in the manner pictured, and that there are peculiarities in the carbon-atom which render such a form of action possible: benzene, in fact, according to this view, may be represented by a double ring. It would appear that when an additive compound is formed the inner cycle of affinity suffers disruption, and, such a cycle being no longer possible, the contiguous carbon-atoms to which nothing has become attached of necessity acquire the ethylenic or unsaturated condition.

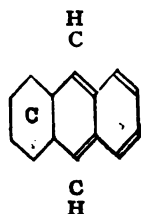
An extension of the hypothesis to naphthalene was suggested in September last year in a paper read at the British Association meeting at Newcastle (*B. A. Report*, 1889, 175). The following is the symbol there proposed:—



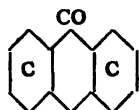
This symbol again involves the admission of the unusual conception that an affinity can act in two directions (cf. *Phil. Mag.*, June, 1888), the two carbon-atoms common to the two nuclei being represented as exerting an influence in both nuclei. In this case also the "centric" affinities are regarded as acting within a cycle composed, however, of 10 carbon-atoms; but no separation of the central carbon-atoms, such as Bamberger suggests, is supposed to have taken place. It becomes possible on this hypothesis, in a measure, to understand that a radicle in the one nucleus should, as is known to be the case, exercise an influence in a radicle in the other nucleus.

It appears to have hitherto been supposed that anthracene has a symmetrical structure: the author contends,

however, that this is not the case, and that it is to be represented by the formula

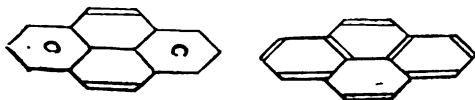


wherein C is the centric nucleus of benzene; but anthraquinone—which, strictly speaking, is derived from dihydroanthracene and not from anthracene—is symmetrical and contains two centric benzene nuclei, thus:—



The behaviour of anthracene and anthraquinone appears to be entirely in accordance with these conclusions. Phenanthrene may be regarded as composed of two lateral "centric" nuclei, to which is conjoined a median nucleus in which the only two "available" carbon-atoms are in the ethylenic condition.

The behaviour of anthracene is more nearly that which it may be supposed the hypothetical hydrocarbon having the structure indicated by Kekulé's benzene symbol would manifest. Pyrene, probably, is still more closely related to the ethylenic form of benzene, and has little, if any, resemblance to the centric form. Two formulæ may be assigned to this hydrocarbon.



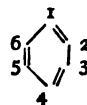
The first of these is the symbol of a phenanthrene derivative; but the behaviour of pyrene is so entirely unlike that of phenanthrene that it may be regarded as out of the question; the second would appear to be entirely in accordance with the results of Bamberger's researches.

It is contended that the formulæ now suggested serve to explain the exceptional physical properties of hydrocarbons such as anthracene and pyrene.

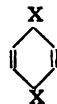
DISCUSSION.

Dr. JAPP desired to know what precise mechanical conception Dr. Armstrong wished to express by the broken bonds in his centric formula. They appeared to denote attractive forces which stopped half way—in other words, attractive forces which did not attract. In this way the centric formula would resolve itself into a benzene hexagon with triadic carbon.

Professor RAMSAY said that he did not see the necessity of substituting an unusual conception for the one in common use, which, in his opinion, gave a sufficient and clear mental picture of the relations between benzenoid compounds. In the case of crotonic and isocrotonic acids, an isomeric change is known whereby the position of the "double bond" is shifted. The difficulty in unreservedly accepting Kekulé's benzene formula, caused by the fact that two ortho-compounds are unknown, while they are required by his conception, was, to some extent, removed by Kekulé himself by his supposition that the double bonds were not stationary, but were sometimes between carbon-atoms 1 and 2, and sometimes between 2 and 3. In order to explain the fact that a change from the symbol—



to the symbol—



is possible, it may be conceived that so long as no external influence is exerted on the benzene ring, it has the constitution suggested by Kekulé. It is probable that two isomeric ortho-compounds are impossible, because, if formed by substitution of hydrogen-atoms 1 and 2, a change would take place whereby the double bond, connecting 1 with 2, would be dissolved and replaced by a single bond, while the double bonds would then exist between 1 and 6, 3 and 2, and 5 and 4. Or the contrary may be the case, and the single bond may be the more unstable form of union, in which case, if an ortho-compound were formed between 2 and 3, the position of the bonds would also be reversed. The case of a change of position of double bonds in the crotonic acids renders this hypothesis not untenable.

Mr. CROMPTON agreed with Professor Ramsay in his remarks, and thought that objections to the Kekulé symbol, based on the view that, because this symbol contained double bonds, benzene should behave as an olefinic compound, were unjustifiable. A double bond was nothing more than an incomplete representation, on paper, of an unsaturated condition or want of equilibrium in the molecule, a state of things that might be due to totally different and distinct causes in the two cases. The behaviour of benzene in this respect must, therefore, differ from that of ethylene. The difference would have to be looked for in the different configurations of the molecules; but it was just this point that received no representation, or only an inadequate one, in the plane formulæ at present in use. The problem would, no doubt, only be finally solved when satisfactory space formulæ for these compounds had been discovered.

In reply to Dr. Japp, Dr. ARMSTRONG said that the broken bonds were intended to figure as resultants, much as the conjoined effect of two forces acting from different directions was expressed by their resultant. Referring to Professor Ramsay's remarks, he expressed the opinion that the isomerism of the crotonic acids was not sufficiently understood to serve as an argument in such a case. However well the non-existence of isomeric ortho- and meta-derivatives might be accounted for by Kekulé's oscillation hypothesis, it was impossible in this way to explain the fact that benzene, on the whole, behaved as a saturated and not as an ethylenic compound; there was also no reason to suppose, as Mr. Crompton had suggested, that "double bonds" in a ring would behave differently from those in an open chain: the whole of v. Baeyer's recent work was in contradiction to any such assumption, and Thomsen's and other observations left little doubt that in the formation of benzene there is a considerable "outgoing of affinity" beyond that which takes place when ethylenic union is effected. He scarcely thought that the introduction of geometric considerations would materially advance the solution of the problem under discussion. Whatever the ultimate fate of his hypothesis, he was convinced that a settlement of many practical problems—those relating to laws of substitution and isomeric change, for example—required the knowledge of the inner structure of the cycloid hydrocarbons; and such speculations, even if proved to be entirely false, at least served to suggest fresh lines of experimental inquiry, and on this account were not only permissible, but also desirable.

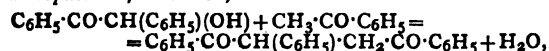
49. "Tertiary Butyl Mercaptan." By LEONARD DOBBIN, Ph.D., Chemical Laboratory of the University of Edinburgh.

The author finds that when tertiary butyl iodide is digested at a gentle heat with a sufficient quantity of zinc sulphide, an interaction takes place which results in the formation of tertiary butyl mercaptan. It is a colourless, extremely volatile liquid which boils at 65–66°, possessing an overpowering disagreeable smell, recalling that of other mercaptans; it solidifies in a freezing mixture of snow and salt to a white semi-translucent mass; it forms white insoluble compounds with mercuric chloride and with silver nitrate.

Products of higher boiling-point are formed at the same time as the mercaptan; these are believed to be triisobutylene, and probably also tertiary butyl sulphide. This part of the subject is under investigation.

50. "Desylacetophenone." By ALEX. SMITH, B.Sc., Ph.D., Chemical Laboratory of the University of Edinburgh.

The author finds that a dilute solution of potassium cyanide in alcohol and water acts in many cases as a condensing agent. By boiling equimolecular proportions of benzoin and acetophenone in dilute alcohol with very little potassium cyanide, a condensation product, *desylacetophenone*, is formed,—



which is the saturated compound corresponding to Japp's anhydracetophenone-benzil. It may be got perfectly pure and white by re-crystallisation from acetic acid and alcohol. It melts at 126°. It is easily transformed into *triphenylfurfurane*, *triphenylpyrrole*, and *triphenylthiophen*, showing its constitution to be that given above. It forms a mono- and a di-hydroxime; by its interaction with one molecular proportion of phenylhydrazine, two molecular proportions of water being given off, an oiazone (pyridazine) is formed. This latter compound is converted by excess of phenylhydrazine into $\alpha\alpha'\beta\beta'$ -N-tetraphenylpyrrole.

A large quantity of another substance having the formula $\text{C}_{29}\text{H}_{22}\text{O}_2$ is formed at the same time as the desylacetophenone. It would seem that the benzoin, or a part of it, acts as a benzaldehyde,—



From acetone and benzoin the only substance isolable, if not, indeed, the only one formed, is that corresponding to the last-mentioned product from acetophenone. It has the formula $\text{C}_{24}\text{H}_{20}\text{O}_2$. The properties and constitutions of these two substances are still under investigation, as are also some other applications of the new interaction.

NOTICES OF BOOKS.

Alkali Works Regulation Act, 1881. Twenty-sixth Annual Report on Alkali, &c., Works by the Chief Inspector. Proceedings during the Year 1889, presented to the Local Government Board and to the Secretary for Scotland. London: Eyre and Spottiswoode.

THE Chief Inspector, in his introduction, refers to a difference between the inspection carried on under this Act and that conducted by sanitary inspectors under the Public Health Act. In this latter case "the senses of smell and sight are sufficient to determine whether a nuisance exists, "though the toleration which ballast-burning in urban districts still enjoys is proof positive that men's notions on the definition of a nuisance are not uniform. The inspector under the Alkali Act has to determine the quality and quantity of any noxious gas found to be escaping, to ascertain if it exceeds the limits of tolerance, and the best practicable means of

minimising its emission. The Act, it must be observed, does not force the manufacturer to use any particular means for the suppression of the nuisance. The inspector, however, frequently finds it his duty to suggest and advise. "He cannot consistently complain of the imperfections in an operation unless he can show the possibility of attaining a better result. To this end he must possess a wide, a varied, and a profound chemical knowledge combined with abundant tact." As he, further, cannot well avoid becoming acquainted with the details of construction of the plant in the works inspected, and with the entire *modus operandi*, an inspector who sells or otherwise reveals trade secrets which have thus come under his cognisance certainly merits very severe punishment. German legislation, we must add, is pointing in this direction.

The number of works which come within the purview of the Act is declining. There are in England 116 alkali works, and in Scotland 16; other works scheduled in the Act, 787 in England and 113 in Scotland, making a total of 1032 registered works. This shows a decrease in the alkali works of 3, and in other scheduled works of 20, making, in England alone, a decrease of 23. The number of separate processes under inspection is increasing, as several distinct processes are often carried on in one establishment and by one and the same firm or company. It is interesting to find that the amount of hydrochloric acid vapour from the decomposition of salt is distinctly below one-half of the statutory limit. As regards the acid gases escaping from the lead chambers, they are below one-third of the legal limit, and are still diminishing yearly. The acids given off from chemical manure works is also decreasing. In 1883 the proportion was 0.5 grain SO_2 per cubic foot; it is now 0.349 grain, and in one district (East Lancashire and Yorkshire) reached 0.2 grain.

One firm only, manufacturers of ammonium sulphate, has been prosecuted under the Act.

The salt industry has decreased upon the whole by about 12 per cent, in consequence, doubtless, of the rise in price inaugurated by the "salt-ring." The production in Durham has, however, increased by 50 per cent.

The consumption of salt in the Leblanc soda process is slightly less than in 1888, viz., 584,203 tons as against 585,498 tons. Meantime, the proportion of salt consumed in the ammonia process is steadily increasing.

The production of ammonium sulphate is gradually increasing. Its value, taken at £12 per ton, has now risen to £1,500,000 yearly, and in the opinion of the Chief Inspector, this quantity might be increased ten-fold.

The recovery of sulphur from the vat-waste of the Leblanc process is now an established fact. The Chance process is in successful operation in twelve alkali works, although the plant required is very costly. There is little prospect of a permanent reduction of the sale price of sulphur. Were it to be lowered, many of the Sicilian mines would doubtless be closed. The amount of tank-waste deposited has now ceased to increase, but some time must elapse before the old heaps and their attending nuisance can disappear.

The influence of certain modern appliances in developing the intelligence of the workmen is fully acknowledged. As instances are mentioned the black-ash revolver, the gas-furnace, and the apparatus used in the recovery of sulphur by the Chance process.

Attempts are being made to suppress, or at least lessen, the injurious effects of salt works, the fumes from which, in the district of Winsford, have devastated the country for miles. Reference is here made to the value of the triple effect principle, by which, in many cases where evaporation is carried on, a vast saving of fuel and consequently of nuisance is effected. This system has been adapted to the salt manufacture by Dr. Pick, of Galicia, and is now being introduced at Shirleywich, in Staffordshire.

A Manual of Pharmaceutical Testing for the Man of Business and his Assistant; comprising Simple Instructions for the Testing of the Chemicals of the "British Pharmacopœia" with such Materials and Appliances as are in common use at the Dispensing Counter. By BARNARD S. PROCTOR, F.I.C. London: Offices of the *Chemist and Druggist*.

THE position of the pharmacist as regards his customers and the medical faculty is greatly changed. Time was when he could manufacture in his back shop or store-rooms the few and simple chemicals required in his business. Hence he might be supposed to know without special testing the quality of the articles in his jars and bottles and drawers. Now he is compelled to purchase from the manufacturer and the wholesale dealer. It is self-evident that he cannot afford to take for granted the skill, the care, and above all the honesty of those who supply him. Hence he is bound, in obedience to the reasonable requirements of the law, no less than in justice to the public, the medical profession, and to his own reputation, to examine all articles which come into his hands. It may possibly be thought that the ordinary manuals of analytical chemistry, qualitative and quantitative, will fully answer the requirements of the case. This, however, is a mistake. The Pharmacopœia lays down certain standards to which all chemicals sold by the chemist and druggists and used in medicine or in making up prescriptions must conform. Our author indicates the simplest, speediest, and most inexpensive manner of ascertaining if these requirements are obeyed. Whether a chemical is absolutely pure—in many cases a vain undertaking under the circumstances—he does not inquire. So long as no substance is present which would interfere with their efficacy, and so long as their strength or degree of concentration is practically correct, he is satisfied, and in so doing he is justified. "There are," he tells us, "sundry cases in which any deviation from the B. P. tests would not be legitimate, there is no alternative but to follow that process." In other cases simpler tests are given where those laid down in the B. P. are unsatisfactory, and certain errors, clerical or typographical, are pointed out. Thus, the instruction to add silver nitrate and barium chloride to an acidified solution of potassa is duly explained as an error.

All things being considered, we hold that there is not merely room, but actual need, for Mr. Proctor's treatise. It is of great importance for the pharmacist, especially in the outset of his professional career, to know when he has fulfilled all righteousness, and is consequently safe and can await the visits of any inspector with equanimity. We cordially echo the author's hope that this hand-book will encourage the habit of testing the chemicals used in medicine, and we believe that it will prove a safe and useful guide.

CORRESPONDENCE.

A RAPID METHOD FOR THE DETERMINATION OF ALUMINIUM IN IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—Take 10 grms. of the iron or steel and dissolve the same in a mixture of 50 c.c. of strong HCl and 30 c.c. of water in a No. 8 beaker; when dissolved add 5 c.c. of a saturated solution of sodium phosphate, then 100 c.c. of water. To this solution add dilute ammonia until the free acid is neutralised; then take up the precipitate carefully with dilute HCl until the solution becomes clear, afterwards add 2 c.c. (not more) of strong HCl and boil; whilst boiling pour in 50 c.c. of a saturated solution of sodium hyposulphite; cover over and boil for one hour. Filter, wash well with hot water, afterwards wash the residue

from filter into the same beaker in which it was boiled, and dissolve in 100 c.c. of a 10 per cent solution of HCl, boil and filter off the sulphur. Evaporate filtrate to 5 c.c., then wash into a platinum dish, and neutralise with pure sodic hydrate (made from sodium). After neutralising add 2 grms. sodic hydrate in excess and boil for 30 minutes, dilute and filter from the iron, after washing the filtrate is made acid with HCl; then precipitate the aluminium down with ammonia; boil, filter off the aluminium phosphate, which is then dissolved in a small quantity of HCl and evaporated to dryness to separate the silica. Re-dissolve in HCl and filter, to the filtrate add 5 c.c. of ammonium phosphate, then ammonia with a few drops of ammonium acetate, and boil for 30 minutes; filter and wash residue well with hot water containing a little ammonium phosphate, ignite, and weigh the precipitate as $AlPO_4$, which contains 22.358 per cent aluminium.

This process, though appearing complicated, can be easily executed in six hours.—I am, &c.,

CHARLES PHILLIPS.

Phillips and Barker,
Chemical and Metallurgical Laboratories,
Fitzalan Square, Sheffield,
June 17, 1890.

UNAUTHORISED REPORTS.

To the Editor of the Chemical News.

SIR,—While reading the article on "Analytical Touts" (CHEM. NEWS, vol. xli., p. 195) the thought crossed me that it is not uncommon to find "pithy and concise reports, productive of excellent business results," manufactured from the simple returns of chemists who would not willingly mislead. Even the titles appended to one's name are at times subject to most curious enlargement. Having recently made a report to a company doing business some two thousand miles from here, I was favoured with a copy of the same in printed form. Judge of my surprise at seeing myself rated (in addition to my legitimate position in this institution) as "Chemist to the Board of Health of the State of New York" and "Consulting Chemist to the United States Government."—I am, &c.,

W. P. MASON.

Rensselaer Polytechnic Institute,
Department of Analytical Chemistry,
Troy, N.Y., June 10, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 23, June 9, 1890.

Action of Alkalies and Alkaline Earths, of Alkaline Silicates, and of Certain Saline Solutions, upon Mica. Production of Nepheline, Sodalite, Amphigene, Orthose, and Anorthite.—Charles and Georges Friedel.—Only few experiments have been hitherto made upon the transformations which rocks and minerals have undergone under the influence of the various agents, physical or chemical, which must have been in action during geological periods. They have therefore thought it interesting to submit the minerals which form rocks to the action of water, with the addition of a certain quantity of alkalies, earths, silicates, and salts at high temperatures, reproducing thus the conditions which have been produced in Nature. They have used a thick tube of steel, lined with platinum, which, when two-thirds full of water, may be heated to about 500°. The subject of the experiments has been mica, and the result has been the production of the minerals mentioned above, i.e., five of the minerals found in the eruptive blocks of Somma.

The Isomeric Conditions of Chromium Sesquibromide. The Blue Sesquibromide.—A. Recoura.—The solid blue bromide, if kept for some time at 100°, is transformed into its green isomer without a change of composition. It does not appear to be produced spontaneously at ordinary temperatures. If a solution of the blue bromide is left to crystallise there are formed, at first, long blue crystalline needles; then when the water has almost disappeared we see appear, among these needles, small green crystals which gradually pervade the entire mass. On the other hand, a saturated solution of the green bromide remains green, and in time deposits green crystals. If a solution of the green bromide, mixed with free hydrobromic acid, is let stand, it remains green for an indefinite time, and does not pass into the violet modifications.

Separation and Determination of Zinc in Presence of Iron and Manganese.—J. Riban.—(See p. 307).

Composition of Clays and Kaolins.—Georges Vogt.—The author's researches show that no process of levigation enables us to separate the hydrated aluminium silicate from the foreign bodies which accompany it. The alkalies contained in clays may have been introduced either by micas or by felspars.

Synthesis of the Carbon Fluorides.—C. Chabrie.—The author has obtained methylene fluoride, CH_2F_2 . He obtains this gas by heating to 180°, for half an hour, 1.7 grms. methylene chloride with 5.08 grms. silver fluoride prepared by Gore's process, and rendered anhydrous with the precautions described by Guntz.

Products of the Saccharification of Starchy Matter by Acids.—G. Flourens.—In opposition to Gruber, O'Sullivan, Brown, and Heron, the author concludes that there is produced in the action of acids upon starch only a single dextrine, as admitted by Payen, which is accurately determined by its high rotatory power, which approaches that of soluble fecula.

Decomposition of Organic Manures in the Soil.—A. Muntz.—In this paper the following conclusions are reached:—In the soils which are incapable of nitrification in consequence of their chemical constitution, the nitrogen of the organic matters is converted into ammonia. The same result happens in soils when nitrification is checked by compactness or where the nitric ferment has been killed. Even when the nitric fermentation is very energetic organic manures give rise to ammonia.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xxi., No. 2.

Two New Sugars extracted from Quebracho.—C. Tanret.—Both these papers have been already noticed.

Volumetric Determination of Tannin in Wines.—NM. Roos, Cusson, and Giraud.—(Already inserted).

A Falsification of Milk.—Dr. Perron.—In order to baffle the use of the lactobutylometer, a novel fraud has been devised. Some oil of low sp. gr., and not possessing a bad taste, is emulsified with yolk of egg and added to the milk after the cream has been abstracted.

Fustus Liebigs Annalen der Chemie.
Vol. ccliv., Part 3.

On the Euxanthon Group.—C. Graebe.—The author has produced euxanthon synthetically by heating 5 grms. resorcylic acid and 6 grms. hydroquinoncarbonic acid with 12 parts of acetic anhydride to a boil for four hours in a small retort with an ascending condenser. The product was then submitted to distillation. Acetic acid and anhydride passed over, and the last portions of the anhydride contained a little euxanthon. On heating more strongly the bulk of the euxanthon sublimed over, whilst much carbon remained in the retort. The syn-

thetic euxanthon has the same composition and properties as the natural kind obtained from Indian yellow.

Communications from the Agricultural-Chemical Laboratory of the University of Göttingen.—Papers by Dr. H. J. Wheeler and B. Tollens on xylose or wood-sugar, a second pentaglucose, and researches on wood-gum.

Communications from the Chemical Institute of Marburg.—Researches by W. Roser on narcotine.—Narcotine is a meconine hydrocartonine, and, like hydrastine, is closely connected with another opium alkaloid, papaverine. Both opium alkaloids are derivatives of a benzyloquinoline. Narceine has no connection with narcotine.

On Benzoyl-tannin.—Dr. Carl Böttlinger.—(Already inserted).

Action of Ammonia and Ethylendiamine upon Tetrachloridiacetyl.—S. Levy.—Not susceptible of useful abstraction.

ERRATUM.—P. 162, col. 1, for "Francis Wallis" read "Francis Watta."

THE BANKHALL OIL AND CHEMICAL WORKS, LIMITED (Formerly Thacker and Co.), LIVERPOOL

FOR SALE BY PRIVATE TREATY as a going concern the above old-established and well-known Oil and Chemical Works, including the whole of the Machinery and Plant and the Goodwill of the business. The Works stand on about 15,530 square yards of land, which is held on lease for seventy-five years from April 30, 1885, at a ground rent of £700 per annum. In addition there is a good private road on the East side of the Works which is occupied jointly with the Lancashire and Yorkshire Railway Co. The situation of the Works is everything that could be desired. They are bounded on the south and east by the Lancashire and Yorkshire Railway, on the west by the Leeds and Liverpool Canal, and on the north by Bankhall Street. There are sidings into the Works from the Lancashire and Yorkshire Railway, and there is also direct access to the Canal. The Works are also in close proximity to the Docks and to the London and North-Western, Midland, and Manchester, Sheffield, and Lincolnshire Railway Stations, and are only about 1½ miles from the Liverpool Exchange. An important feature in connection with these Works is that they are not liable to be restrained or prosecuted for emitting noxious odours, &c. The Buildings comprise extensive Oil and Cake Mills, with Elevator, Oil and Tallow Refineries, Oil Stores, Tar and Naphtha Distilleries, Soapery, large Warehouses, with very extensive Fireproof Vaults and Steam Hoist, Cooperage, Stables, and the usual Offices. The Machinery and Plant are comparatively new, in excellent condition, and capable of doing a very extensive manufacturing business. The business connection is a most valuable one. With a view to a speedy realisation a very moderate price will be accepted.

For orders to inspect the Works and to treat apply to the Liquidator, T. THEODORE ROGERS, 30, North John Street, Liverpool, or to Wm. F. MORECROFT and CO., Solicitors, 5, Castle Street, Liverpool.

COUNTY BOROUGH OF SALFORD.
(GAS DEPARTMENT).

TAR.

The Gas Committee invite Tenders for the purchase and removal of the surplus Tar to be produced at their Bloom Street, Regent Road, and Liverpool Street Works in twelve months from July 13th next.

The approximate quantity will be 4,500 tons.

Forms of tender and conditions of contract may be obtained on application to the Gas Engineer, Gas Offices, Bloom Street, Salford. Sealed tenders, endorsed "Tender for Tar," addressed to the Chairman of the Gas Committee, must be delivered to me on or before Thursday, the 10th prox., at 5 o'clock in the evening.

By order,

SAMUEL BROWN, Town Clerk.

Town Hall, Salford,
June 12, 1890.

TAR.

The Directors of the Nuneaton Gas Company invite Tenders for the surplus TAR to be produced at their works for one year from the 1st of July next. Quantity about 150 tons. Tenders, sealed and endorsed, must reach me not later than the 10th July.

JOHN H. BLAND, Secretary.

Nuneaton, 19th June, 1890

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FOAM.*

By the Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D.,
F.R.S., Professor of Natural Philosophy, R.I.

WHEN I was turning over in my mind the subject for this evening, it occurred to me to take as the title of the lecture, "Froth." But I was told that a much more poetical title would be "Foam," as it would so easily lend itself to appropriate quotations. I am afraid, however, that I shall not be able to keep up the poetical aspect of the subject very long; for one of the things that I shall have most to insist upon is that foaming liquids are essentially impure, contaminated—in fact, dirty. Pure liquids will not foam. If I take a bottle of water and shake it up, I shall get no appreciable foam. If, again, I take pure alcohol, I get no foam. But if I take a mixture of water with 5 per cent. of alcohol there is a much greater tendency. Some of the liquids we are most familiar with as foaming, such as beer or ginger-beer, owe the conspicuousness of the property to the development of gas in the interior, enabling the foaming property to manifest itself; but of course the two things are quite distinct. Dr. Gladstone proved this many years ago by showing that beer from which all the carbonic acid had been extracted in vacuo still foamed on shaking up. I now take another not quite pure but strong liquid, acetic acid, and from it we shall get no more foam than we did from the alcohol or the water. The bubbles, as you see, break up instantaneously. But if I take a weaker acid, the ordinary acid of commerce, there is more, though still not much, tendency to foam. But with a liquid which for many purposes may be said to contain practically no acetic acid at all, seeing that it consists of water with but 1-1000th part of acid, the tendency is far stronger: and we get a very perceptible amount of foam. These tests with the alcohol and acetic acid are sufficient to illustrate the principle that the property of foaming depends on contamination. In pure ether we have a liquid from which the bubbles break even more quickly than from alcohol or water. They are gone in a moment. In some experiments I made at home I found that water containing a small proportion of ether foamed freely; but on attempting two or three days ago to repeat the experiment, I was surprised to find a result very different. I have here some water containing a very small fraction of ether, about 1-240th part. If I shake it up, it scarcely foams at all; but another mixture made in the same proportion from another sample shows more tendency to foam. This is rather curious, because both ethers were supposed to be of the same quality; but one had been in the laboratory

longer than the other, and perhaps contained more greasy matter in solution.

Another liquid which foams freely is water impregnated with camphor. Camphor dissolves sparingly; but a minute quantity of it quite alters the characteristics of water in this respect. Another substance, very minute quantities of which communicate the foaming property to water, is glue or gelatine. This liquid contains only 3 parts in 100,000, of gelatine, but it gives a froth entirely different from that of pure water. Not only are there more bubbles, but the duration of the larger bubbles is quite out of proportion to that of water bubbles. This sample contains 5 parts in 100,000, nearly double as much; but even with but 1 part in 100,000, the foaming property is so evident as to suggest that it might in certain cases prove valuable for indicating the presence of minute quantities of impurities. I have been speaking hitherto of those things which foam slightly. They are not to be compared with, say, a solution of soap in water, which, as is well known to everybody, froths very vigorously. Another thing comparable to soap, but not so well known, is saponine. It may be prepared from horse chestnuts by simply cutting them in small slices and making an infusion with water. A small quantity of this infusion added to water makes it foam strongly. The quantity required to do this is even less than in the case of soap; so the test is more delicate. It is well known that rivers often foam freely. That is no doubt due to the effect of saponine or some analogous substance. Sea-water foams, but not, I believe, on account of the saline matter it contains; for I have found that even a strong solution of pure salt does not foam much. I believe it has been shown that the foaming of sea-water, often so conspicuous, is due to something extracted from seaweeds during the concussion which takes place under the action of breakers.

Now let us consider for a moment what is the meaning of foaming. A liquid foams when its films have a certain durability. Even in the case of pure water, alcohol, and ether, these films exist. If a bubble rises, it is covered for a moment by a thin film of the liquid. This leads us to consider the properties of liquid films in general. One of their most important and striking properties is their tendency to contract. Such surfaces may be regarded as being in the condition of a stretched membrane, as of india-rubber only with this difference, that the tendency to contract never ceases. We may show that by blowing a small soap bubble, and then removing the mouth. The air is forced back again by the pressure exerted on the bubble by the tension of the liquid. This ancient experiment suffices to prove conclusively that liquid films exercise tension.

A prettier form of the same experiment is due to Van der Mensbrugghe, who illustrated liquid tension by means

* A Lecture delivered at the Royal Institution of Great Britain, March 28, 1890

of a film in which he allowed to float a loop of fine silk, tied in a knot. As long as the interior of the loop, as well as the exterior, is occupied by the liquid film, it shows no tendency to take any particular shape: but if, by insertion of, say, a bit of blotting paper, the film within the loop be ruptured, then the tension of the exterior film is free to act, and the thread flies instantaneously into the form of a circle, in consequence of the tendency of the exterior surface to become as small as possible. The exterior part is now occupied by the soap film, and the interior is empty. Many other illustrations of this property of liquids might be given, but time does not permit.

In the soap film, as in the films which constitute ordinary foam, each thin layer of liquid has two surfaces; each tends to contract; but in many cases we have only one such surface to consider, as when a drop of rain falls through the air. Again, suppose that we have three materials in contact with one another,—water, oil, and air. There are three kinds of surfaces separating the three materials, one separating water and oil, another oil and air, and a third surface separating the water from the air. These three surfaces all exert a tension, and the shape of the mass of oil depends upon the relative magnitudes of the tensions. As I have drawn it here (Fig. 1), it is implied that the tension of the water-air surface is less than the sum of the other two tensions—those of the water-oil surface and the air-oil surface; because the two latter acting obliquely balance the former. It is only under such conditions that the equilibrium of the three materials as there drawn in contact with one another is possible. If the tension of the surface separating water and air exceeded the sum of the other two, then the equilibrium as depicted would be impossible. The water-

FIG. 1.



air tension, being greater, would assert its superiority by drawing out the edge of the lens, and the oil would tend to spread itself more and more over the surface.

And that is what really happens. Accurate measurements made by Quincke and others show that the surface tension separating water and air is really greater than the sum of the two others. So oil does tend to spread upon a surface of water and air. That this is the fact we can prove by a simple experiment. At the feet of our chairman, our Honorary Secretary, is a large dish, containing water which at present is tolerably clean. In order to see what may happen to the surface of the water, it is dusted over with fine sulphur powder, and illuminated with the electric light. If I place on the surface a drop of water, no effect ensues; but if I take a little oil, or better still a drop of saponine, or of soap-water, and allow that to be deposited upon the middle of the surface, we shall see a great difference. The surface suddenly becomes dark, the whole of the dust being swept away to the boundary. That is the result of the spread of the film, due to the presence of the oil.

How then is it possible that we should get a lens-shaped mass of oil, as we often do, floating upon the surface of water. Seeing that the general tendency of oil is to spread over the surface of water, why does it not do so in this case? The answer is that it has already spread, and that this surface is not really a pure water surface at all, but one contaminated with oil. It is in fact only after such contamination that an equilibrium of this kind is possible. The volume of oil necessary to contaminate the surface of the water is very small, as we shall see presently; but I want to emphasize the point that, so far as we know, the equilibrium of three surfaces in contact with one another is not possible under any other conditions,

That is a fact not generally recognised. In many books you will find descriptions of three bodies in contact, and a statement of the law of the angles at which they meet; that the sides of a triangle, drawn parallel to the three intersecting surfaces must be in proportion to the three tensions. No such equilibrium, and no such triangle, is possible if the materials are pure; when it occurs, it can only be due to the contamination of one of the surfaces. These very thin films, which spread on water, and, with less freedom, on solids also, are of extreme tenuity; and their existence alongside of the lens proves that the water prefers the thin film of oil to one of greater thickness. If the oil were spread out thickly, it would tend to gather itself back into drops, leaving over the surface of the water a film of less thickness than the molecular range.

One experiment by which we may illustrate some of these effects I owe to my colleague, Professor Dewar. It shows the variation in the surface tension of water, due to the presence on it of small quantities of ether. I hold in my hand masses of charcoal, which can be impregnated with ether. The greater part of the surface of the charcoal is covered with paraffin wax, and, in consequence, the ether which has already penetrated the charcoal can only escape from it again on one side. The result is that the water in the rear of this boat of charcoal will be more impregnated with ether than the part in front, so the mass of charcoal will enter into motion, and the motion will extend over a considerable interval of time. As long as the ether remains in sufficient quantity to contaminate the water in the rear, so long is there a tendency to movement of the mass. The water covered with the film of ether has less tension than the pure water in front, and the balance of tensions being upset, the mass is put in motion. If the nature of the case is such that the whole surface surrounding the solid body is contaminated, then there is no tendency to movement, the same balance in fact obtaining as if the water were pure.

Another body which we may use for this purpose is camphor. If we spread some camphor scrapings on a surface of pure water, they will, if the surface is quite clean, enter into vigorous movement, as you now see. This is because the dissolved camphor diminishes the surface tension of the water. But if I now contaminate the water with the least possible quantity of grease, the movements of the camphor will be stopped. I merely put my finger in, and you observe the effect. There is not much poetry about that! A very slight film, perfectly invisible by ordinary means, is sufficient so to contaminate the water that the effect of the dissolved camphor is no longer visible.

I was very desirous to ascertain, if possible, the actual thickness of oil necessary to produce this effect, because all data relating to molecules are, in the present state of science, of great interest. From what I have already said, you may imagine that a quantity of oil required is very small, and that its determination may be difficult. In my experiments,* I used the surface of water contained in a large sponge bath three feet in diameter. By this extension of the surface, I was able to bring the quantity of oil required within the range of a sensitive balance. In Diagram 2, I have given a number of results obtained at various dates, showing the quantity of oil required to produce the effects recorded in the fourth column. Knowing the weight of the oil deposit, and the area of the water surface upon which it was uniformly spread, it was easy to calculate the thickness of the film. It is seen that a film of oil about $\frac{1}{4}$ millionth of a millimetre thick is able to produce this change. I know that large numbers are not readily appreciated, and I will therefore put the matter differently. The thickness of the oil film thus determined as sufficient to stop the motions of the camphor is one-fourth of the wave length of yellow light. Another way of saying the same thing is that this thickness of oil bears to one inch the same ratio that one second of time bears to half a year.

* *Proc. Roy. Soc.*, March, 1890.

DIAGRAM 2.

A Sample of Oil somewhat Decolourised by Exposure.

Date.	Weight of Oil.	Calculated Thickness of Film in Micro-millimetres.	Effect upon Camphor Fragments.
	M.grm.		
Dec. 17..	0.40	0.81	No distinct effect.
Jan. 11..	0.52	1.06	Barely perceptible.
Jan. 14..	0.65	1.32	Not quite enough.
Dec. 20..	0.78	1.58	Nearly enough.
Jan. 11..	0.78	1.58	Just enough.
Dec. 17..	0.81	1.63	Just about enough.
Dec. 18..	0.83	1.68	Nearly enough.
Jan. 22..	0.84	1.70	About enough.
Dec. 18..	0.95	1.92	Just enough.
Dec. 17..	0.99	2.00	All movements very nearly stopped.
Dec. 20..	1.31	2.65	Fully enough.
<i>A Fresh Sample.</i>			
Jan. 28..	0.63	1.28	Barley perceptible.
Jan. 28..	1.06	2.14	Just enough.

When the movement of the camphor has been stopped by the addition of a minute quantity of oil, it is possible, by extending the water surface enclosed within the boundary, without increasing the quantity of oil, to revive the movements of the camphor; or, again, by contraction to stop them. I can do this with the aid of a flexible boundary of thin sheet brass, and you see that the camphor recovers its activity, though a moment ago it was quite dead. It would be an interesting subject for investigation to determine what is the actual tension of an oily surface contaminated to an extent just sufficient to stop the camphor movements; but it is not an easy problem. Usually we determine surface tensions by the height to which the liquids will rise in very fine tubes. Here, however, that method is not available, because if we introduce a tube into such a surface, there is no proof that the contamination of the inner surface in the tube is the same as that prevailing outside. Another method, however, may be employed which is less open to the above objection, and that is to substitute for the very fine or capillary tube, a combination of two parallel plates open at their edges. We have here two such plates of glass kept from absolutely closing by four pieces of thin metal* inserted at the corners, the plates being held close against these distance-pieces by suitable clamps. If such a combination be inserted in water, the liquid will rise above the external level, and the amount of the rise is a measure of the surface tension of the water. You see now the image on the screen. A is the external water surface; B is the height of the liquid contained between the glass plates, so that the tension may be said to be measured by the distance AB. If a little oil be now deposited upon the surface, it will find its way between the plates. The fall which you now see shows that the surface tension has been diminished by the oil which has found its way in. A very minute quantity will give a great effect. When the height of the pure water was measured by 62, a small quantity of oil changed the 62 into 48, and subsequent large additions of oil could only lower it to 38. But after oil has done its worst, a further effect may be produced by the addition of soap. If Mr. Gordon now adds some soap, we shall find that there is a still further fall in the level, showing that the whole tension now in operation is not much more than one-third of what it was at first. This is an important point, because it is sometimes supposed that the effect of soap in diminishing the tension of water is due to merely the formation upon the surface of a layer of oil formed by decomposition of the soap. This experiment proves the contrary, because we find that soap can do so much more than oil. There is indeed, something more or less corresponding to the decomposition of the soap and the formation of a superficial layer of oil. But the decomposition takes place in a very peculiar

manner, and under such conditions that there is a gradual transition from the soapy liquid in the interior to the oily layer at the top, and not, as when we float a layer of oil on water, two sudden transitions, first from water to oil, and secondly from oil to air. The difference is important, because, as I showed some years ago, capillary tension depends on the suddenness of change. If we suppose that the change from one liquid to another takes place by slow stages, though the final change may be as before, the capillary tension would absolutely disappear.

There is another very interesting class of phenomena due to oil films, which I hope to illustrate, though I am conscious of the difficulty of the task,—namely, the action of oil in preventing the formation of waves. From the earliest times we have records of the effect of oil in stilling waves, and all through the Middle Ages the effect was recognised, though connected with magic and fanciful explanations. Franklin, than whom, I suppose, no soberer inquirer ever existed, made the thing almost a hobby. His attention was called to it accidentally on board ship from noticing the effect on the waves caused by the greasy debris of a dinner. The captain assured him that it was due to the oil spread on the water, and for some time afterwards, Franklin used to carry oil about with him, so as never to miss a chance of trying an experiment. A pond is necessary to illustrate the phenomena properly, but we shall get an idea of it by means of this trough six feet long, containing water.† Along the surface of the water we shall make an artificial wind by means of a fan,‡ driven by an electro-motor. In my first experiments I used wind from an organ bellows, which is not here available. Presently we shall get up a ripple, and then we will try the effect of a drop of oil put in to windward. I have now put on the drop, and you see a smooth place advancing along. As soon as the waves come up again, I will repeat the experiment. While the wind is driving the oil away, I may mention that this matter has been tested at Peterhead. Experiments were there made on a large scale to show the effect of oil in facilitating the entrance of ships into harbour in rough weather. Much advantage was gained. But here a distinction must be observed. It is not that the large swell of the ocean is damped down. That would be impossible. The action in the first instance is upon the comparatively small ripples. The large waves are not directly affected by the oil; but it seems as if the power of the wind to excite and maintain them is due to the small ripples which form on their backs, and give the wind, as it were, a better hold of them. It is only in that way that large waves can be affected. The immediate effect is on the small waves which conduce to that breaking of the large waves which from the sailor's point of view is the worst danger. It is the breaking waters which do the mischief, and these are quieted by the action of the oil.

I want to show also, though it can only be seen by those near, the return of the oil when the wind is stopped. The oil is at present driven to one end of the trough;‡ when the wind stops it will come back, because the oil film tends to spread itself uniformly over the surface. As it comes back, there will be an advancing wave of oil; and as we light the surface very obliquely by the electric lamp, there is visible on the bottom of the trough a white line, showing its progress.

Now, as to the explanation. The first attempt on the right lines was made by the Italian physicist, Marangoni. He drew attention to the importance of contamination upon the surface of the water, and to its tendency to spread itself uniformly, but for some reason which I cannot understand, he applied the explanation wrongly.

* The width is 8 inches, and the depth 4 inches. The sides are of glass; the bottom and ends of wood, painted white.

† For this fan and its fittings the Institution is indebted to the liberality of the Blackman Ventilating Company.

‡ May, 1890. Any moderate quantity of oil may be driven off to leeward; but if oleate of soda be applied, the quieting effect is permanent.

More recently Reynolds and Aitken have applied the same considerations with better success. The state of the case seems to be this:—Let us consider small waves as propagated over the surface of clean water; as the waves advance, the surface of the water has to submit to periodic extensions and contractions. At the crest of a wave the surface is compressed, while at the trough it is extended. As long as the water is pure there is no force to oppose that, and the wave can be propagated without difficulty; but if the surface be contaminated, the contamination strongly resists the alternate stretching and contraction. It tends always, on the contrary, to spread itself uniformly; and the result is that the water refuses to lend itself to the motion which is required of it. The film of oil may be compared to an inextensible membrane floating on the surface of the water, and hampering its motion; and under these conditions it is not possible for the waves to be generated, unless the forces are very much greater than usual. That is the explanation of the effect of oil in preventing the formation of waves.

The all-important fact is that the surface has its properties changed, so that it refuses to submit to the necessary extensions and contractions. We may illustrate this very simply by dusting the surface of water with sulphur powder, only instead of dispersing the sulphur, as before, by the addition of a drop of oil, we will operate upon it by a gentle stream of wind projected downwards on the surface, and of course spreading out radially from the point of impact. If Mr. Gordon will blow gently on the surface in the middle of the dusty region, a space is cleared;* if he stops blowing, the dust comes back again. The first result is not surprising, but why does the dusty surface come back? Such return is opposed to what we should expect from any kind of viscosity, and proves that there must be some force directly tending to produce that particular motion. It is the superior tension of the clean surface. No oil has been added here, but then no water surface is ever wholly free from contamination; there may be differences of degree, but contamination is always present to some extent. I now make the surface more dirty and greasy by contact of the finger, and the experiment no longer succeeds, because the jet of wind is not powerful enough to cleanse the place on which it impinges; the dirty surface refuses to go away. or if it goes in one direction it comes back in another.

(To be continued).

NOTE ON THE RECENT CONSTRUCTION OF THREE MODIFIED FORMS OF VOLTAIC CELLS.

By H. N. WARREN, Research Analyst.

THE first voltaic cell of which I wish to make mention, and which is used practically in the same manner as an ordinary Bunsen cell, consists of a zinc outer cylinder excited by dilute sulphuric acid, but enclosing a porous pot containing a saturated solution of arsenic acid in place of the nitric acid of commerce. The circuit is completed by inserting into the acid a carbon rod, the connections being made in the usual manner. The battery evolves a constant supply of electricity, the electromotive force being about 1½ volts, the reaction terminating with the production of arsenious acid, and the solution of an equivalent proportion of zinc. This form of cell evolves no noxious odours similar to what is experienced when using the nitric acid battery, but unfortunately, owing to a somewhat osmotic passage of the arsenious acid into the outer vessel, it occasions a danger of forming arseniuretted hydrogen through coming into contact with the zinc cylinder. To overcome this danger naturally necessitates

the placement of the same either out of doors or where a good draught can be assured.

The second cell or bromine battery, another modification of the first, differing only in minute details, is comprised by adopting for the round porous pot that of the flat form, and bounded on either side by flat plates of zinc; the inner cell being furnished with a platinum plate in place of the graphite rod, and excited by water which has been saturated with bromine, a small excess of the latter being also allowed to remain at the bottom of the cell in order to replenish the waste. The cell when in full action affords a constant current of electricity, the chief secondary compound formed being apparently hydrobromic acid, the bromine of which may be again set free by the addition of a small quantity of bleaching-powder.

The third, a modification of the copper sulphate battery, which has taken the name of the asbestos battery, not that that substance plays any decided action as regards an exciting agent, but serves admirably to prevent too intimate a contact between the copper and zinc plates. The battery may be arranged either single or compound, and if the latter be desired, consists in arranging a various number of zinc coils coated both sides with asbestos paper, and bound over in close proximity with thin copper foil; the coils may be for convenience sake arranged by placing one inside the other, the battery being excited by immersing the whole in a saturated and acidified solution of copper sulphate, the supply being maintained by an ordinary receiver containing a further quantity of crystals. The action of the asbestos may be thus readily explained. When to a solution of copper sulphate containing a coil of metallic copper, there is introduced one of zinc for a few moments, a most energetic action is set up, which nevertheless soon terminates with the deposition of metallic copper; this exciting power thus established owing to the small space allowed between the asbestos and the zinc, and at the same time the excellent conducting power of the large surface of copper exposed on either side of the zinc plates, immediately conveys any current which would otherwise be lost on to the terminus.

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NOTES ON QUANTITATIVE ANALYSIS.*

By L. H. FRIEDBURG, Ph.D.

THE following chapters make but little claim to originality, and treat only of well-known facts. But as every chemist during a long period of analytical occupation develops for himself a particular *modus operandi*, based upon results obtained, it is proper to recommend what he deems to be valuable. In this sense I offer the following descriptions given below, omitting all reference to literature or authorship of the different methods; premising only that not one is described that I have not myself frequently used.

A.—ACIDIMETRY AND ALKALIMETRY.

The test liquids used are hydrochloric acid and ammonium hydrate. It is customary to prepare normal or decinormal solutions. With solids, provided they are pure, this may be arrived at to a degree of accuracy practically sufficient. With solutions of gases, such as HCl or NH₃, the preparation of a normal solution, even if performed with the greatest care and the best standardised measuring vessels or specific gravity apparatus, we cannot omit quantitative determination of at least one of the liquids prepared. The following figures will show that in trying to prepare normal solutions of the aforesaid liquids a difference of 0.1957 per cent of HCl and 0.0740

* This experiment is due to Mr. Aitken.

* From the *Journal of the American Chemical Society*, vol., xii., No. 5.

per cent of nitrogen were quantitatively determined. For very accurate work such determination ought to be made, and no attempt to normalise afterwards by dilution or concentration is necessary or desirable. The measuring of new quantities of liquids is a source of new errors at best. The sacrifice of the advantage of rapid final calculation of results with such solutions is well balanced by greater accuracy obtained.

900 c.c. hydrochloric acid, *puriss.*, sp. gr. 1.20, were mixed with about 8000 c.c. of distilled water, while 450 c.c. of the commercially pure strong ammonium hydrate were added to about 6400 c.c. of dist. water. The mixtures were allowed to stand for a week. Then it was ascertained how these two liquids would neutralise each other by volume. The whole length of the burettes was used, and in the last determination they were filled up again. It was found, using cochineal as an indicator, that:—

- a. 20 c.c. HCl were neutralised by 25 c.c. NH_4OH .
- b. 20 " " " " 25 " NH_4OH .
- c. 20 " " " " 24.95 c.c. NH_4OH .

20 c.c. HCl therefore corresponded to 25 c.c. NH_4OH .

Next, three different weighed quantities of HCl were taken and neutralised (using the same indicator) with ammonia. The results were:—

- a. 19.7861 grms. HCl required 24.30 c.c. NH_4OH ;
consequently, 1 grm. HCl required 1.228 c.c. NH_4OH .
 - b. 5.8800 grms. HCl required 7.20 c.c. NH_4OH ;
therefore, 1 grm. HCl required 1.224 c.c. NH_4OH .
 - c. 15.4551 grms. HCl required 19.00 c.c. NH_4OH ;
or, 1 grm. HCl required 1.229 c.c. NH_4OH .
- 1 grm. HCl, therefore, was neutralised by 1.23 c.c. NH_4OH .

Finally, three chlorine determinations were made. The silver chloride was dried as usual, but only that part of it which would spontaneously leave the filter when emptied into the porcelain crucible was determined as horn silver; the filter and the remaining amount were burned in a weighed platinum spiral until the silver was reduced to a metallic state, adhering as a little knob to the wire, which was again weighed. Following are the results:—

- a. 0.9710 grms. HCl gave 1.66603 grms. AgCl, equal to 0.42362 HCl.
- b. 1.8240 grms. HCl gave 0.3023 grms. AgCl, equal to 0.0769 HCl.
- c. 7.8802 grms. HCl gave 1.31663 grms. AgCl, equal to 0.33478 HCl.

From these analyses the following amounts of HCl in one grm. of the liquid were calculated:—

- a. 1 grm. HCl contains 0.04249 grm. HCl gas.
- b. 1 grm. HCl contains 0.04218 grm. HCl gas.
- c. 1 grm. HCl contains 0.042485 grm. HCl gas.

A noticeable loss having occurred in the determination b, the average of a and c was taken; 1 grm. HCl contains 0.04249 gaseous HCl. The difference between the average taken from all three determinations, and of that from the two mentioned, however, is only 0.0001 grm.

From all the above it follows that:—

- 1 grm. HCl solution is neutralised by = 1.23 c.c. NH_4OH solution.
- 1 grm. HCl solution contains = 0.04249 gr. HCl gas.
- 1 c.c. NH_4OH solution contains = 0.013264 grm. nitrogen.
- 1 c.c. NH_4OH solution is neutralised by = 0.8 c.c. HCl solution.
- 1 c.c. HCl solution contains = 0.034543 grm. HCl gas.
or = 0.033596 grm. chlorine.

These solutions were prepared in February, 1888. The HCl solution was kept in a large flask with doubly perforated rubber stopper, one hole of which allowed the escape of the liquid by means of a syphon (or self-feeding burette), while the second opening was connected with a small flask containing a few c.c. of the same liquid as the large one. The ammonia bottle was closed with a doubly perforated cork. A small flask, containing a little liquid of the same strength, a second small flask, which is kept empty, and finally a cylinder containing cotton, solid KOH, and again cotton, are attached, in the above sequence, to one opening, the other serving for the outlet of the liquid.

These liquids are kept standing in the laboratory, not exposed to direct sunlight, but subject to the natural variations of temperature during the year. Nevertheless, they have not changed during these last two years under the given conditions. To-day, as two years ago, 20 c.c. of the HCl solution is saturated by 25 c.c. of the ammonia solution, while both solutions, when used in a nitrogen determination of urea which had been six times re-crystallised and finally dried over sulphuric acid, then heated with soda-lime, was shown to have retained the previously determined percentage, the urea analysis yielding figures of *absolute* correctness.

(To be continued).

THE ELECTROMOTIVE FORCE OF METALLIC SALTS.*

By CLARENCE L. SPEYERS.

(Concluded from p. 294).

In the following tables the column headed *v* contains the number of litres of water in which a grm. equivalent of the salt has been dissolved, that headed E. F. the corresponding electromotive force in volts (10^8 C. G. S.), and that headed Δ the difference between successive values of E. F. Any deviation from the mean exceeding 1 per cent is noted in the tables. The observations have all been duplicated, and sometimes quadruplicated.

Until more data have been accumulated, the above results cannot be most intelligently discussed, but a glance at the tables will show a few interesting facts.

1. The electromotive force always increases on dilution; the increment of nitric, acetic, and sulphuric acids is very slight, it is true, but still sufficiently marked, in the opinion of the writer, to be unmistakable. At any rate, there is no diminution, and therefore the equivalent electromotive force (electromotive force $\times$ equivalent weight, due account being taken of the quantity contained in the liquid) increases rapidly.

2. Hydrochloric acid has a much lower value than the other three acids, which form a group by themselves, with approximately equal values. It may appear strange that this acid should have an electromotive force so much inferior to that of acetic acid, but the agreement of repeated measurements indicated that they were correct.

3. The electromotive force of a mixture of equal equivalents of an acid with hydrochloric acid is not the mean of the two values, but is only slightly greater than that of hydrochloric acid. The increment also belongs to this acid. Nitric, acetic, and sulphuric acids have an electromotive force so nearly alike that no conclusion can be drawn from their mixtures.

4. Turning to the zinc salts, we find a drop in electromotive force of 33(Cl), 59(NO_3), 166(Ac), and 129(SO_4) millivolts. The first observed values, $\frac{1}{2}$ equivalent, are compared. The increment, however, has been increased. As the solutions are diluted, the fall due to substitution of zinc for hydrogen appears to approach that observed with chlorine, 33 millivolts.

SUPPLEMENT TO THE CHEMICAL NEWS, JANUARY 9, 1891.

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO
PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY
WILLIAM CROOKES, F.R.S., &c.

VOLUME LXII.—1890.

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AND SOLD BY ALL BOOKSELLERS;

—
MDCCCXC.

by h the weight of resin contained in a weight = 100 of the mixture, we have—

For the mixture of linseed oil in refined resin oil $[\alpha]_D = + \frac{1}{2} h$; ditto linseed oil and selected white oil, $[\alpha]_D = + \frac{1}{2} h$; ditto linseed oil and fine rectified oil, $[\alpha]_D = + \frac{1}{2} h$. The first mixture is that which is most commonly met with. In practice it is sufficient to measure $[\alpha]_D$ with the polarimeter or to value h in refined resin oil according to the formula $h = [\alpha]_D \frac{1}{\frac{1}{2}}$.

As the oils in question are deeply coloured it is better to operate in a tube of 10 c.m., and to calculate h by the formula $h = \alpha_D \frac{1}{\frac{1}{2}}$.

2. *Assay of a Paint.*—To detect oil of resin in commercial paint we operate as follows:—

a. We put in a flask a certain quantity of paint, add ether, agitate and let settle. The ether having dissolved the paint floats at the top. The tube of the polarimeter is filled with the ethereal solution. If the rotation observed is null, the resin oil is present. In the contrary case, if $[\alpha]_D$ is the rotation to the right measured for the thickness of 20 c.m., a study of the rotatory power of the ethereal solutions of resin oil and of linseed oil mixed with resin oil has shown that the proportion of resin oil added may be calculated by the formula—

$$h = \frac{[\alpha]_D}{43^1}$$

b. We put in a flask a weight p_1 of the ethereal solution; we heat to 100° in the water-bath so as expel the ether; the oil, which only boils about 300°, remains in the flask; let p_2 be its weight. We determine thus the proportion—

$$\frac{p_1}{p_2} \times 100 = h,$$

for 100 of the oil (linseed oil and resin oil) contained in the ethereal solution examined with the polarimeter.

If $h_1 = h$ we may conclude that the paint contains oil of resin without linseed oil.

In the ordinary case h_1 is greater than h ; then—

$$\frac{h}{h_1} \times 100$$

will be the percentage of resin oil contained in the linseed oil which has been used in making up the paint.—*Comptes Rendus*, vol. cx., p. 1273.

RECENT SYNTHETICAL EXPERIMENTS IN THE SUGAR SERIES.*

PROFESSOR EMIL FISCHER'S researches on the sugars of the glucose group have been remarkably successful, and recently he has effected the synthesis of both dextrose and levulose. A year ago, in the *American Chemical Journal*,† the experiments were described by means of which he had succeeded in preparing a new synthetical sugar, which he called acrose, and which was found to be an isomer of dextrose and levulose. Acrose possesses all the general properties of dextrose and levulose, and only differs from these natural sugars in being optically inactive. Fischer has now succeeded in determining the constitution of acrose, and in his recent papers‡ he has shown that it is the inactive modification of levulose. It bears the same relation to ordinary levulose that racemic acid bears to ordinary tartaric acid; and just as racemic acid can be split into dextro- and levo-tartaric acids, so from acrose ordinary levulose and a new levulose having an equal but opposite rotatory power can be obtained.

The obstacles that are encountered in this kind of work are very great, and one can gain some idea of the diffi-

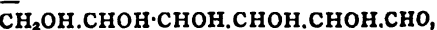
culty of determining the constitution of a sugar by remembering that, according to the Le Bel-Van't Hoff hypothesis,* a compound with four asymmetric carbon atoms like dextrose can exist in sixteen stereometric forms. Nevertheless Fischer has not only determined the constitution of acrose and effected the synthesis of levulose, but he has also discovered the inactive and the levo-modifications of mannite and of the new sugar, mannose. He has shown that mannose and dextrose have the same constitution and that one may be converted into the other. He has further prepared all these substances synthetically, and, what is also of very great importance, he has developed and perfected the methods of transforming the sugars and their derivatives into one another to such an extent that the synthesis of the remaining members of the glucose group will probably be effected in the near future. In fact, so great are the additions to our knowledge resulting from these researches that Fischer's work may well be said to mark the beginning of a new epoch in the history of the carbohydrates.

Mannose.

This new sugar was discovered by Fischer‡ in studying the oxidation-products of the poly-acid alcohols with the aid of phenylhydrazine. It is obtained, together with levulose, by the oxidation of mannite with nitric acid, and it can readily be distinguished from the other sugars on account of the insolubility of its hydrazone. Mannose has the composition represented by the formula $C_6H_{12}O_6$, and is therefore isomeric with dextrose and levulose, and, like these, it reduces Fehling's solution, and undergoes fermentation when mixed with yeast. It is optically active, and turns the plane of polarised light to the right, but not so strongly as dextrose. Its specific rotatory power is $+12.96$, that of dextrose being $+58.7$. Reduction with sodium amalgam converts it into mannite. Mannose has not yet been obtained in crystalline condition. The white solid sugar deliquesces rapidly in moist air, and is extremely easily soluble in water. It dissolves with difficulty in absolute alcohol, and is insoluble in absolute ether. Like dextrose and levulose, mannose can be converted in furfural and levulinic acid. Treatment with bromine-water converts it into mannonic acid, an isomer of gluconic acid.

But the distinguishing characteristic of mannose is its behaviour with phenylhydrazine. The cold aqueous solution of the sugar, when treated with phenylhydrazine, gives at once a crystalline precipitate of mannose phenylhydrazone, whereas the hydrazones of dextrose and levulose and the other sugars are readily soluble in water. When heated with more phenylhydrazine, the mannose hydrazone is converted into an osazone, which is identical in all its properties with phenylglucosazone, the compound that is obtained from dextrose and levulose under similar circumstances. As glucosazone can be converted into levulose, it is therefore possible by this means to transform mannose into levulose.

*Constitution of Mannose.**—As mannose differs in properties from both dextrose and levulose, it was at first supposed that its constitution was different from that of either of these sugars. Thus, the formula of dextrose being—



and that of levulose—



the formula—



suggested itself for mannose. In order to obtain experimental evidence either for or against this formula, mannose was treated with hydrocyanic acid, according to Kiliani's§ method of determining the constitution of

* Van't Hoff. "Dix Années dans l'Histoire d'une Théorie," p. 54.

† *Ibid.*, xxi., 1805; xxii., 365.

‡ *Ber. d. Chem. Ges.*, xxii., 365.

§ *Ibid.*, xxi., 916.

* *American Chemical Journal*, xli., 257.

† *Ibid.*, xi., 277.

‡ *Ber. d. Chem. Ges.*, xxiii., 372, 376.

sugars. Direct addition took place, and from the resulting compound mannose-carbonic acid was obtained. This acid, upon reduction with hydriodic acid, was converted into normal heptioic acid. This result indicates that the constitution of mannose cannot be represented by the formula given above, because a sugar whose constitution is represented by that formula would by this process have been converted into an isoheptioic acid. But the fact that normal heptioic acid was obtained indicates that mannose contains an aldehyd group, and that its constitution must be expressed by the same formula as that which represents the constitution of dextrose. Mannose and dextrose are, therefore, physical isomers. To explain this isomerism recourse must be had to the Le Bel-Van't Hoff hypothesis, according to which it is possible to foresee the existence of eight optically active and eight inactive compounds of the formula of dextrose. Both compounds are dextro-rotatory, but as one of them turns the plane of polarised light to a much greater extent than the other, Fischer at first supposed that dextrose and mannose were optical isomers, that they were the dextro- and levo-modifications of the same structural system, and that the rule which usually holds in such cases, namely, that the one isomer turns as far to the left as the other to the right, was modified in this case in some unknown manner by the remaining asymmetric carbon atoms. This supposition was not confirmed by subsequent experiments, for, as will be shown below, another mannose similar in all its properties to the one here described, but possessing an equal but opposite rotatory power, was obtained from arabinose carbonic acid.

Reduction of the Acids of the Sugars.*

Before proceeding to describe how the optical isomer of mannose was obtained, it is necessary to call attention to a reaction which is of some importance, and which is a general one for the acids of the sugar series. Ordinarily the carboxyl group of organic acids cannot be reduced to the aldehyd group by means of nascent hydrogen. This reduction, however, takes place readily, as has been discovered by Fischer, in the case of the sugar acids that yield lactones. If gluconic acid lactone, for example, be treated with sodium amalgam, and the solution be acidified from time to time, it soon acquires the power of reducing Fehling's solution, and by continued action a solution of sugar is obtained. The solution contains dextrose, and when it is treated with phenylhydrazine it gives glucosazone. In the same way mannonic acid, obtained by the oxidation of mannose with bromine-water, was reduced with sodium amalgam and mannose again obtained. Other sugar acids behaved in the same way—in short, the method appears to be a general one, and one of very great importance in connection with the synthesis of the sugars. It is possible by means of this method, together with Kiliani's reaction, to build up a sugar from one containing a smaller number of carbon atoms. For, by treating a sugar with hydrocyanic acid, an addition-product is obtained from which an acid containing one carbon atom more than the original sugar can be prepared. This acid can then be reduced with sodium amalgam, and thus converted into the corresponding sugar. The process of lengthening the chain of carbon atoms can then be repeated. Thus far only acids that form lactones have been reduced with sodium amalgam, and it appears that this property is in some way connected with the power of forming lactones.

(To be continued).

Electrolysis of Aluminium Fluoride by Igneous Fusion.—Adolphe Minet.—The author has operated upon aluminium fluoride, and has obtained from one horse-power an hourly production of 30 gms. aluminium. —*Comptes Rendus*, vol. cx., No. 23.

* Ber. d. Chem. Ges., xxii., 2204.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

June 20, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the Chair.

Prof. A. W. WORTHINGTON made a communication on "*The Stretching of Liquids.*"

The three known methods by which this may be effected, viz., the barometer tube method, the centrifugal method, and the method of cooling, were described, and the precautions necessary in filling the tubes and in freeing the liquids from air discussed. With non-volatile liquids, such as sulphuric acid, the tubes are put in communication with a good pump, and before sealing, the liquid in the tube is kept at a higher temperature than that in the communicating vessel, in order that a stream of vapour may be passing outwards and carry with it any air liberated from the glass during the process of sealing.

Before using tubes by the centrifugal method the author finds it advantageous to subject them to considerable "jarring" at intervals. This usually breaks the liquid column and liberates a small bubble of air, which may then be floated out. By repeating this many times, the adhesion of the liquid is greatly increased. With these precautions he had subjected water to a tension of 7.5 and sulphuric acid to 12 atmospheres. The cooling method of Berthelot (*Ann. de Chimie*, xxx., 1852) was then tried. In this method the liquid nearly fills a strong closed glass tube at a particular temperature. On slightly heating it expands and fills the whole tube, any residual air being dissolved. On cooling again, the liquid remains extended and still fills the tube, until at last it lets go with a violent "click," and the bubble of residual air and vapour reappears. The tension of the liquids tested under these circumstances have usually been calculated from the relative change of volume on the assumption that the coefficient of extensibility is the same as that of compressibility.

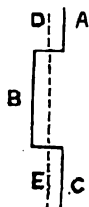
The author exhibited and described an apparatus by which the tension and the extension can be measured simultaneously. The tension is ascertained from the enlargement of the ellipsoidal bulb of a thermometer sealed into the containing vessel, and the extension calculated from the volume of the bubble after the click. The tension thermometer had been calibrated by internal pressure, and in determining the extension correction is made for the change of volume of the apparatus. By this method he had subjected alcohol to a tension of 17 atmospheres, and found that the coefficient of extensibility is much less than that of compressibility. It is not clear as to what causes the liquid to let go of the glass, but it is found that the bubble can be caused to reappear by passing an electric current through a wire sealed in the capillary tube.

Sir Wm. THOMSON remarked that Prof. Worthington's paper was a curious commentary on the usual mathematical definitions of "a liquid," as a substance which offered no resistance to being separated into parts. Speaking of freeing liquids from air, he said the beneficial effect of jarring could easily be shown by tapping an ordinary "philosophical hammer"; separation of the column always leaves a bubble, which can then be floated off. He had also found that in freeing liquids from air by boiling it was advantageous to have a long escape tube, so that part of the liquid condenses and runs back.

Mr. C. V. BOYS read a paper on "*The Measurement of Electro-magnetic Radiation,*" by himself, Messrs. A. E. BRISCOE, and W. WATSON.

When Mr. Gregory described his new electric radiation-meter on Nov. 1, 1889, one of the authors said that the observed effect might be due to some cause other than expansion by heating, and that if it was a true heating

effect it might be measured thermally. The present communication describes experiments undertaken to investigate the question. The first method employed was developed from the idea that if two fine wires be placed near together, and both act as resonators to a primary oscillator, the electro-dynamic attraction caused by the electric currents up and down the wires and the electrostatic repulsion between the charges on them, might result in the relative motion of the two wires. From theoretical considerations, based on the assumptions that the currents are harmonic in time and space, the authors inferred that the electro-dynamic effect would preponderate at the middle of the wires, whilst the electrostatic repulsion would be greater at the ends. To cause the attractions and repulsions to conspire in producing rotation cranked resonators, A B C (see fig.) were made; one



was fixed and the other suspended by a quartz fibre, to turn about a middle line, D E. These were enclosed in a glass vessel, and on starting the oscillator a turning movement was observed in a direction opposite to that expected. This motion was eventually traced to the electrostatic influence of the oscillator, for although the imperfectly conducting surface of the glass acted as a perfect screen from such action when the potentials of the oscillation were varied slowly, it did not do so for changes occurring about 500,000,000 times per second. After adopting means to avoid this disturbance, and constructing lighter resonators, the experiments were repeated with negative results. From the dimensions of the quartz fibre used it was estimated that a force of 158-1,000,000ths of a grain could have been detected with certainty; this would have corresponded to about 1-300th of an ampère in each resonator. It is hoped that by further increasing the sensitiveness of the apparatus and using parabolic reflectors the effect sought for may be detected.

In the second method of attacking the subject, a Joule's dynamic air-thermometer was employed. This consisted of a glass tube with a partition along the middle extending nearly to the ends. If one side of the tube be warmed, convection currents circulate and deflect an index placed in the stream. A small mirror suspended about one edge and counterpoised was used for an index, and was so sensitive that it was impossible to get the air still enough by any ordinary method of screening. However, by the ingenious device of putting the thermometer within a larger tube kept rotating by clockwork, the difficulties were surmounted. A doubled wire placed in one side of the thermometer served as resonator, and on starting the oscillator a large deflection resulted. A similar deflection was caused by applying about $\frac{1}{2}$ of a volt to the ends of the wire. This proved that the effect observed by Mr. Gregory is due to heating. The least rate of heating observable with the air thermometer was found to correspond to 1 calorie (gramme-water-centigrade) per 24 hours in the whole tube, or 1 calorie per centimetre of wire in 103 days.

Dr. LODGE asked Sir William Thomson whether, when electric pulses travel along parallel wires with the velocity of light, any action could exist between them, for two charged spheres travelling together at that velocity exert no mutual attraction or repulsion.

In reply, Sir WILLIAM said he was inclined to think Mr. Boys' treatment of the subject was in the main correct, but it was quite possible that at such velocities the

ordinary laws might be modified by the fact that the time taken for the force to be propagated from wire to wire is comparable with that required for the pulse to travel the whole length of the wire. As an example of the peculiar effects of rapid discharges he said he had seen two copper wires which had been flattened against each other by lightning.

Mr. BOYS thought that in his resonators a condition analogous to stationary waves would exist, for the pulses are reflected from the ends.

Dr. LODGE said he had that afternoon observed the action of parallel strips when Leyden-jar discharges were passed through them. The strips gave a kick at each discharge.

Mr. GREGORY mentioned that in trying to increase the sensitiveness of his meter so as to measure the variation with distance, he had found that two resonators in proximity interfered with each other. He had, however, succeeded in increasing the sensibility about five-fold.

Prof. WORTHINGTON asked if it was possible to measure the energy of the oscillator, and also whether the quantity caught by the resonator could be estimated from the solid angle it subtended at the source of energy, wherever that might be.

Prof. PERRY considered it easier to infer the energy of the source from that received by the resonator.

Dr. LODGE said the energy of the source could be easily measured. The power radiated was enormous whilst it lasted, vastly exceeding that of tropical sunshine; if it could be made continuous, the apparatus would soon be red hot. The energy radiated, he said, converges on the resonators, and hence the solid angle method of estimating the amount received would be erroneous. Moreover, the source was not at the oscillator, but at a quarter wave-length from it, and most of the energy returns to the oscillator; only a small fraction is splashed off and sent into space. Small oscillators radiate powerfully because the quarter wave-lengths are small; whereas the slow oscillators, or alternators used commercially, radiate very little of their energy. The exact law of variation of intensity of radiation with distance was rather complicated, but the theory had been completely worked out by Stokes in 1848.

Mr. BLAKESLEY thought the energy that returns to the oscillator would be available for subsequent radiations.

Dr. LODGE pointed out that wires or other resonators placed within the quarter wave-length would intercept part of the returning energy.

Two communications, "*Notes on Secondary Batteries*," by Dr. GLADSTONE and Mr. HIBBERT, and "*An Easy Rule for Calculating Approximately the Self-Induction of a Coil*," by Prof. PERRY, were taken as read.

In the first of these the authors show cause for believing that the beneficial effect produced by adding sodium sulphate to the ordinary electrolyte is due partly to its facilitating the reduction of lead sulphate and also to its power to diminish local action between the electrolyte and different parts of the lead plates. As regards the chemical actions which take place during the working of ordinary cells, they see no reason to doubt the view put forward by one of them in 1882, that the substance produced in the voltaic reaction is ordinary lead sulphate, $PbSO_4$. They also conclude that the high E.M.F. of a cell immediately after stopping the charging current is due to the inequality of acid strength near the two plates, and the gradual fall of E.M.F. is caused by the equalisation of strength produced by diffusion.

Prof. PERRY's rule relates to hollow cylindrical coils, and is expressed by the following formula:—

$$L \text{ (in secohms)} = \frac{n^2 a^2 \div 10^7}{1.844a + 3.1c + 3.5b}$$

Where n = number of windings.

a = mean radius of winding in centimetres.

b = axial length.

c = radial depth of winding,

and b and c are less than $\frac{a}{2}$.

The time-constant of such a coil is given in terms of the volume of copper (V) in cubic centimetres by—

$$\frac{L}{R} = \frac{V \div 1000}{0.728a + 1.33c + 1.5b}$$

and the conditions for making this small are pointed out in the paper.

A paper by the Rev. T. Pelham Dale was postponed till next meeting.

NOTICES OF BOOKS.

The Extra Pharmacopœia: with the additions introduced into the British Pharmacopœia, 1885. By W. MARTINDALE, F.C.S.

Medical References, and a Therapeutic Index of Diseases and Symptoms. By W. WYNN WESTCOTT, M.B. Sixth Edition. London: Lewis.

British Pharmacopœia, 1885, Addendum, 1890. Summary of Suggestions and List of Articles to be included.

THE authors, in their preface, very judiciously contend that medicines should be combined extemporaneously to suit the disease, instead of, as is now too commonly the case, the patient being treated by ready-made compounds prepared to suit imaginary cases. They give a list of the additions to the British Pharmacopœia made at the revision in 1885, as well as other important changes. It is complained that the range of doses ordered is too limited, the minimum being often too large and the maximum too small.

The last-mentioned pamphlet contains a list of articles recommended for official introduction by the medical authorities—to wit, the Royal Colleges of Physicians and Surgeons of London, the Society of Apothecaries of London, the Royal Colleges of Physicians and Surgeons of Edinburgh, the Faculties of Physicians and Surgeons of Glasgow, the Universities of Edinburgh, Aberdeen, and St. Andrews, the King's and Queen's College of Physicians of Ireland, and the Apothecaries Hall of Ireland.

Practical Chemistry for Medical Students Required at the First Examination of the Conjoint Examining Board in England. By S. RIDEAL, D.Sc., F.I.C., F.C.S., F.G.S. London: H. K. Lewis.

THE work before us is avowedly examinational. It is to furnish the student, or rather the examinee, with just so much knowledge of chemical analysis as will be required from him on one particular occasion. Instructions are given by identifying fifteen metals and seven acids, the former being present "as metal, oxide, sulphides, or simple salts." Mixtures and complex compounds do not lie within the scope of this manual. For the selection of the substances dealt with, the insertion of some and the omission of others, the author is not responsible. He who would be the "guide, philosopher, and friend" of our modern alumni, whether his teachings are *viva voce* or are conveyed through the medium of printers' ink, must not even by implication question the wisdom of "examining boards." Against the "hints for work" and the tests laid down, nothing can be said. But have they not all been already given in works of all sizes and of many prices?

A Novel Method of Preparing Anhydrous Aluminium Chloride.—C. F. Mabery (*Berichte*).—The author causes gaseous hydrochloric acid to act upon an alloy of aluminium and copper. The copper is not attacked.—*Moniteur Scientifique*, March, 1890.

CORRESPONDENCE.

MEDICAL OFFICERS OF HEALTH AND PUBLIC ANALYSTS.

To the Editor of the Chemical News.

SIR,—Referring to Mr. White's letter (*CHEMICAL NEWS*, vol. lxi., page 301), I am sure nobody would think of doubting the ability of men like Drs. Tidy, Stevenson, Hill, and Adams to fill the positions which they respectively hold to the satisfaction of everyone concerned, as these gentlemen have made chemistry a special study, in addition to being thoroughly qualified from a medical point of view.

When I last wrote I had in my mind the above named "Medico-Public Analysts," as well as one or two others of lesser note, but their undoubted efficiency seems to me to emphasize all the more forcibly my contention as regards the incompetency of many candidates for similar positions. The fact is, in filling vacancies of this nature, the chemical aspect of the question is often altogether ignored, or, at any rate, regarded as of secondary importance, it being taken for granted, I suppose, that the work will be done somehow.

An instance occurs to me in which a very unsuitable man was chosen to fill the dual offices of Medical Officer of Health and Public Analyst in a large town in the Midlands. He obtained the appointment, I understand, entirely through local influence.—I am, &c.,

ROWLAND WILLIAMS.

Laboratory and Assay Office,
28, Pall Mall, Manchester.
June 24th, 1890.

ESTIMATION OF ALUMINA IN IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—I notice in your last issue a letter from Mr. Charles Phillips describing a method for the determination of aluminium in iron and steel, and which is substantially the same as that described by Mr. J. E. Stead in a paper read before the Society of Chemical Industry at Newcastle early in December, 1889.

As no mention is made of this paper in your correspondent's letter, I think it only fair to Mr. Stead to call the attention of your readers to his work in this direction.

I enclose you copy of the paper referred to, which I think will clearly show Mr. Stead's priority.—I am, &c.,

C. H. RIDSDALE.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 24, June 16, 1890.

On the Different Isomeric Inosites and on their Heat of Transformation.—M. Berthelot.—The author has found that the two symmetric inosites have substantially the same solution-heats, precisely as is the case with the two symmetrical tartaric acids. The mixture of the two solutions (previously brought to an identical temperature) produces no thermic phenomenon. The neutral inosite, by compensation, shows a solution-heat of -7.47 cals. higher in absolute value than each of the active inosites, a fact identical with that observed in the three corresponding tartaric acids.

Combinations and Reactions of Gaseous Ammonia and of Gaseous Hydrogen Phosphide upon the Halogenous Compounds of Arsenic.—M. Besson.— PH_3 in excess gives, at common temperatures at least, with arsenic bromide and iodide, products analogous to those resulting from the decomposition at 300° of the corresponding ammonium compounds. There is this difference: that as nitrogen has no affinity for arsenic, these two bodies remain isolated, whilst phosphorus and arsenic unite.

A New Method of Forming Crystalline Metallic Oxychlorides. Researches on Copper Oxychlorides.—G. Rousseau.—The author's new method of forming oxychlorides, described in a former communication, is confined to those of tin, antimony, titanium, bismuth, zinc, and iron. On heating for three days to between 180° and 200° , a solution containing 1 mol. copper chloride and 6 mols. of water, he obtained crystallised atacamite. The crystals are very small on operating in presence of marble, but if grobertite is used fine crystals are obtained, identical with those of natural atacamite.

Combination of Phosphorus Pentafluoride with Hyponitric Acid.—Emil Tassal.—Phosphorus pentafluoride yields, with hyponitric acid, an addition compound, NO_4PF_5 , and not substitution-products, as with the corresponding compounds of chlorine. Phosphorus pentafluoride is only decomposed after the prolonged action of very strong induction-sparks. Its resistance to chemical and physical agents should lead to an explanation of the formation of addition-compounds in preference to substitution-compounds.

Formation-heat of Uric Acid and the Alkaline Urates.—C. Martignon.—The formation-heat of uric acid, setting out from its elements, = +148.1 cal.; that of bibasic potassium urate = +256.2 cal.; that of the monobasic potassium salt = +207 cal. For the sodium salts we have 310.9 cal. for the bibasic urate and 237.6 cal. for the monobasic urate. Uric acid should decompose tri- and bibasic sodium phosphates, liberating respectively 4.9 and 0.5 cal., and giving rise to the monobasic phosphate called *acid*. This prevision agrees with experience, and is one of the causes of the acidity of urine. The formation-heat of ammonium urate is = 183 cal.

Chloralimide and its Isomer; a Reversible Isomeric Transformation.—MM. Béhal and Choay.—The isomer in question—*isochloralimide*—is more soluble than its isomer in all organic solvents; it is insoluble in water and melts at at 103° — 104° .

On a Sophistication of Linseed Oil.—A. Aignan.—(See p. 7).

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., March, 1890.

Study of Various Questions of General Chemistry.—A course of lectures by M. Schützenberger delivered at the Collège de France.

Synthesis of Aromatic Amines by Means of Resorcine and Ammonia.—Alphonse Seyewitz.—The author has succeeded in obtaining metaphenylenediamine in this manner, as he proves by a number of reactions. By heating a mixture of resorcine and ammoniacal calcium chloride in a sealed tube to 200° he also obtains a yellow matter of the composition—

C	71.64
H	5.88
N	6.90
O	15.58

100.00

A red colouring-matter obtained during the same reaction gives, upon cotton mordanted with tannin and

antimony, a fast catechu brown having a good lustre. Upon wool prepared with potassium dichromate it gives fine shades which bear fulling. This new colour has several advantages over Bismarck brown.

New Method of Analysis for Industrial Waters which have to Undergo a Chemical Purification and for the Feed-waters of Steam-boilers.—Leo Vignoa.—This process, which refers merely to the hardness of the waters, has been already noticed. The author points out that the carbonic acid in distilled water prepared a few days ago may amount to 5 c.c.

Process for Dissociating Common Salt into Chlorine and Sodium Carbonate by Means of the Electric Current.—W. Hempel.—The products may be kept from reacting on each other by the interposition of a diaphragm between the two electrodes. The diaphragm is composed of a layer of asbestos paste, kept tightly compressed between the two electrodes, which are circular plates, the cathode of iron and the anode of carbon. The current must have at total tension of 5.7 volts. A metric horse-power (980 volt-ampères) produced by a dynamo gives, per hour, 64 grms. chlorine and 25 grms. sodium carbonate.—*Berichte*.

New Mineralogical Deposits at Tarapaca.—C. Ochsenius.—An account of beds of astrakanide and tamarugite in Chile. The particulars may be found in the *Chemiker Zeitung*.

Formation of Hydrogen Sulphide by the Action of Steam upon Lyes of Calcium Hydrosulphate.—H. Deutecom and F. Rothe (*Chemische Industrie*).—This paper cannot be given without the accompanying tables.

Generalities on Glasses.—From *Dingler's Polytechnic Journal*. A series of analyses of different qualities of glass.

A New Optical Glass (Dingler).—A notice of the glass containing phosphoric and boric acids, and used for the object-glasses of microscopes. It is said that by its means magnitudes of 1-820,000 m.m. can be recognised.

The Solubility of Sulphides in Glass.—H. Rich. Zsigmondy.—Previously noticed.

The Oriental Enamel on Bricks and its Imitations.—J. Beck (*Journal für Praktische Chemie*).—Already noticed.

Colouring-Matters.—A series of notes summarised by E. Grandmoulin, of the Chemical School of Mulhouse.

The Industrial Society of Mulhouse.—Session of January 15th, 1890.—M. Descroix, of Villefranche, has used a system of dyeing aniline blacks by "pulverisation." He has abandoned the process on sanitary grounds, as the health of the workmen suffered from the dust of aniline salt and potassium dichromate diffused in the air.

M. Jeanmaire gave some details on the injury to cloth occasioned by iron-mordants. Reducing agents, such as phosphorous and arsenious acids, sodium bisulphite, &c., if added to the mordant, retard the injuries, whilst oxidisers promote them. A cloth which had been worked in ferrous acetate at 5° B. left rolled up for a month and then dunked was weakened to the extent of 60 to 70 per cent. The action was especially manifest after dunging. If cloth is steamed immediately after mordanting it does not suffer, but if it is left folded up and then steamed the attack is manifested.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 12.

Simultaneous Determination of Carbon and Sulphur in Organic Matter.—M. Prunier.—Already inserted.

New Monobromo-camphor.—M. Cazeneuve.

On the Camphamimes, a New Class of Bases derived from Camphor.—M. Cazeneuve.—These two papers have been previously noticed.

On Eucalyptols.—M. Pannetier.—This product is a simple mixture of salicylic acid, of phenol, and of essence of eucalyptus.

Poisoning by an Edible Fungus (*Helvella esculenta*).—B. Studer, M. Demme, and J. Berlinerblau.—The fungus in question belongs to the class of *Ascomycetes*, and is commonly eaten in some parts of Germany. In the case in question its ingestion was followed by colic and vomiting. These effects are traced to the fact that during the desiccation of the mushrooms putrid fermentation had set in, determining the formation of putrefaction-alkaloids.

Vol. xxi., No. 1.

Falsification of Tea in China.—M. Riche.—Certain teas seized at Dunkirk and Paris did not differ decidedly from genuine tea in their ash and in their proportion of tannin. But they gave no crystalline theine at all, but in its stead a greenish viscid substance. It is remarked that the highest percentage of tannin found in this investigation was 16.80.

Falsification of Tea in China.—E. Collin.—The same subject from a morphological point of view. The author gives cuts showing the structural peculiarities of true and spurious teas, both as seen with the naked eye and with the microscope. He remarks that this fraud is more readily detected by means of the lens than by chemical analysis. Every true tea-leaf, of whatever variety, has serrated edges.

On the Castor Oil Seed.—E. Villejean.—M. Stillmarck finds that the residual cake from the extraction of castor oil contains a considerable proportion of a poison which is tasteless, more violent than arsenic, and which cannot be extracted from the human body by any known means. The fatal dose for a man of 60 kilos. is 18 c.m., a quantity found in 3 grms. of the castor-oil cake. This poison, which has received the name *ricinus*, is neither an alkaloid, nor a glucoside, nor an organic acid, but an albumenoid.

Fraudulent Jalap.—M. Flückiger.—The roots of jalap, which in 1842 yielded 17 per cent of resin, now rarely yield more than 12, sometimes only 7.50. The Mexican dealers extract the resin from the roots by treatment with alcohol.

Are the Hyposulphites good Antiseptics?—Prof. Perroncito.—The author shows that cultures of chicken-cholera do not lose their pathogenic properties by being kept for forty-eight hours in contact with solutions of hyposulphite (sodium thiosulphite) at 25 to 50 parts per thousand.

Journal für Praktische Chemie.
New Series, Vol. xli., Nos. 1 and 2.

Researches from the Laboratory of the University of Freiburg.—These researches comprise:—Contributions to the knowledge of the homologues of anthracene and anthraquinone, by Karl Elbs; a memoir by Ad. Claus and M. Posselt on orthooxyquinoline anasulphonic acid; a paper by Ad. Claus and G. Pollitz on α -bromquinoline; and a memoir by Ad. Claus and W. Rüppel on di- β -naphthylene ketone-oxide.

Researches from the Chemical Laboratory of Prof. Alex. Saytzeff at Kasan.—This consists of an investigation of the first oxide of the pentavalent alcohol of diallylcarbinol.

Certain Derivatives of Piazine.—P. W. Arhenius.—An account of the action of chromic acid upon derivatives of diacididihydropiazine and of the dichlordiacipiazines.

Action of Hydroxylamine Hydrochlorate upon Para-dioxyparaquinones.—Fr. Kehrmann and W. Tiesler.—Not adapted for abstraction.

Studies on Diastase.—C. J. Lintner and F. Eckhardt.—The authors conclude that both to gluten and mucidine

there adheres a substance as little known as the diastatic ferment which passes into a ferment on treatment with dilute acid or with water alone. This hypothetical substance may receive the name of fermentogen or zymogen. Bacteria cannot be concerned in the origin of diastase, since they do not exist in the interior of the grains of corn.

Vol. xli., No. 3.

Researches on the Sulphonicamides.—P. Hebenstreit.—The sulphonic cyamides form no acid alkaline salts. We must hence assume that they are distinguished from the other known derivatives of cyanamide by their tendency to polymerisation. The insolubility both of the acids and their salts in ether is noteworthy. The acids obtained are crystalline. The aromatic sulphonic cyamides contain crystalline water, one molecule being so firmly bound that when the acids are decomposed it participates in the formation of the resulting products. Benzol-sulphonic cyamide forms, when heated, benzolsulphonamide, but benzolcyanamide forms when heated a polymer. The sulphonic cyamides are strong acids and form definite salts with bases.

Researches from the Laboratory of the University of Freiburg.—These comprise contributions to a knowledge of the homologues of anthracene and anthraquinone, by K. Elbs; on the sulphonic acids of the normal propylbenzol, by Ad. Claus and O. Weizel; and on para-oxyquinoline-sulphonic acid, by Ad. Claus and M. Posselt.

MISCELLANEOUS

University College, Dundee.—A scholarship, of the value of £30 a year, has just been placed at the disposal of Prof. Percy Frankland at University College, Dundee, St. Andrew's University, by Miss E. F. Forster, of London. It is intended that the student holding the same shall devote the whole of his time to the prosecution of original research. The scholarship, which will be known as "The Forster Scholarship," has been awarded for this year to Mr. John MacGregor, M.A.

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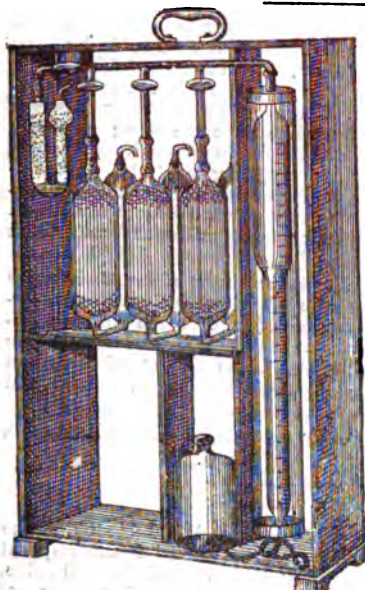
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THE CHEMICAL NEWS.

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RAFFINOSE, MELITOSE, OR MELITRIOSE.*

By ARTHUR R. LING, F.I.C.

IN view of the discussion now going on amongst technical chemists in the sugar industry as to the presence of raffinose† in certain commercial beet-root sugars, notably those recovered from low syrups, I have been induced to compile the following *resumé* of the chemical work which has been done on this compound, there being, so far as I am aware, no such account in English chemical literature at the present time.

The fact that raffinose possesses a high dextro-rotatory power renders its detection and estimation in commercial sugars a matter of *a priori* importance, since the percentage of cane-sugar in the same is invariably determined by the optical test.

The history of the compound commences in the year 1842, when Johnston (*Mem. Chem. Soc.*, i., 159) separated a sugar from a species of eucalyptus indigenous to Tasmania. He ascribed to it the formula $C_{12}H_{28}O_{16}$, and showed that it contained water of crystallisation. It was next examined by Berthelot in 1856 (*Annales chim.* [3], xlv., 66), who gave it the name melitose, and found that it had a specific rotatory power $[\alpha]_D = 88$, that it was converted by the action of dilute acids into a mixture of a fermentable sugar—probably glucose—and a non-fermentable sugar, eucalyn.

Ritthausen, in 1884 (*Four. Pr. Chem.* [2], xxix., 351), and Böhm (*Ibid.*, xxx., 37) obtained a sugar from cotton seed, which the former regarded as identical with Berthelot's melitose, whilst the latter considered it a distinct substance, and called it gossypose.

In the year 1876 Loiseau (*Compt. rend.*, lxxxii., 1058) separated a crystalline sugar from the beet-root molasses of Messrs. Sommer et Cie. which had the composition $C_{18}H_{32}O_{16.5}H_2O$, and possessed a relative rotation to that of cane-sugar, 159 : 100; this he called raffinose. Tollens (*Ber.*, xviii., 26) expressed the view that raffinose was identical with the sugar from cotton-seed, and probably also with Berthelot's melitose, but he confirmed Loiseau's number for the rotatory power. This was finally established by Scheibler (*Ber.*, xviii., 1779) and by Rischbiet and Tollens (*Ibid.*, 2611; *Annalen*, ccxxxii., 169).

O'Sullivan has separated raffinose from barley (*Chem. Soc. Four. Trans.*, 1886, 70), and v. Lippmann (*Ber.*, xviii., 3087; *xxi. Ref.*, 889) has demonstrated its presence in beet-roots themselves.

In his first experiments Tollens (*loc. cit.*) favoured the formula $C_{12}H_{22}O_{11.3}H_2O$ of Berthelot, Ritthausen, and Böhm, inasmuch as he found that raffinose lost about 13 p.c. of water at 100°, and that decomposition begins above this temperature, but it was subsequently shown by Scheibler (*loc. cit.*), that when the compound is dried, first in a partial vacuum over concentrated sulphuric acid for about a fortnight, and then at 100°, a loss of about 15 p.c. of water is attained, which corresponds to that demanded by Loiseau's formula, $C_{18}H_{32}O_{16.5}H_2O$. Rischbiet and Tollens then showed that the amount of

mucic acid obtained on oxidising raffinose with nitric acid was, assuming that the compound yields a third of its weight of galaetose, consistent with Loiseau's formula, but from a consideration of the sodium derivative, which they found contained 6—7 p.c. of sodium, they were led to double this formula. The determinations of the molecular weight made since by Tollens and Mayer (*Ber.*, xxi., 1566) and by Brown and Morris (*Chem. Soc. Four. Trans.*, 1888, 619), who employed Raoult's freezing-point method, as well as that of de Vries (*Compt. rend.*, cvi., 751), who determined the isotonic coefficient, point, however, to the simpler formula.

In molasses rich in raffinose the latter separates out on standing, whilst from such as contains less Scheibler's method (*Ber.*, xviii., 1409) may be employed for its isolation. This consists in converting the mixed sugars into the mono-strontia compounds and cooling, when about 75 p.c. of the cane-sugar separates out as mono-strontia saccharate; the filtrate is boiled with an excess of strontium hydroxide, and the precipitate containing the di-strontia compounds of raffinose and cane-sugar decomposed by a current of carbonic anhydride. The process is then repeated, a syrup being ultimately obtained consisting chiefly of raffinose, the compound being finally purified by crystallisation from alcohol.

Raffinose crystallises in needles or prisms which are almost insoluble in absolute alcohol but very easily soluble in water. Its specific rotatory power is, according to Landolt (*Ber.*, xxi., 198), $[\alpha]_D = 104.5$, which represents the mean of the values obtained by Scheibler, Tollens, Rischbiet and Tollens, v. Lippmann, Loiseau, and Ritthausen. Beythien and Tollens have more recently given the value $[\alpha]_D = 104.4$ (*Annalen*, cclv., 195).

It has been shown by Rischbiet and Tollens (*Annalen*, ccxxxii., 110) that when raffinose is warmed on the water-bath with dilute acids under fixed conditions, the specific rotatory power is reduced to about one-half,* but that if more concentrated acid be employed and the heating continued for a longer time the reduction in rotation reaches one-fifth, with the formation of a certain amount of humus matter (cf. Scheibler and Mittelmeier, *Ber.*, xxii., 1684). This has been confirmed by numerous observers. Rischbiet and Tollens (*Ber.*, xviii., 2611) have shown further that when raffinose is heated for a considerable time with acids, levulinic acid is produced, and have confirmed Berthelot's statement that mucic acid is formed when raffinose is oxidised with nitric acid, the amount obtained under the conditions given being 22—23 per cent of the weight of raffinose.† Raffinose does not reduce Fehling's solution until after heating with acids, and, like cane-sugar, it is stable in alkaline solution. It possesses only a very faint sweet taste. Rischbiet and Tollens (*Annalen*, ccxxxii., 110) have found that raffinose is completely fermentable with yeast. Berthelot (*Compt. rend.*, cix., 548) finds, however, that an active yeast completely ferments it, but a weak yeast only about one-third, whilst Loiseau (*Compt. rend.*, cix., 614) states that fermentation is complete with a low fermentation yeast, but only reaches one-third with a high one. There appears to be no sharp qualitative test for the recognition of raffinose.

The fact that raffinose yields compounds with bases has long been known, and has been specially studied by Scheibler and by Beythien and Tollens (*Ber.*, xxii., 1047; *Annalen*, cclv., 195). Di-strontia raffinose,—



baryta raffinose, $C_{18}H_{32}O_{16.2}BaO$, di-baryta raffinose,

* An abstract of this paper was read at the Conference of Chemists held at the Beetroot Sugar Association's Rooms on June 26, 1890, to consider the methods for the detection and estimation of raffinose.

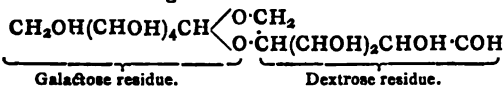
† Throughout this paper I have made use of the name raffinose, since, although the objection that it is based on the misconception that the compound is formed during a process of refining from cane-sugar has been urged against it by several eminent German chemists, it is more generally known in England by this name.

* Scheibler and Mittelmeier (*Ber.*, xxii., 3120) state that a dilute solution of the invertase of yeast has an action at the ordinary temperature similar to that of dilute acids at a higher temperature, whilst a strong solution at 40° determines the complete inversion.

† Assuming that galaetose forms a third part of the total inversion product, since this sugar yields about 75 p.c. of mucic acid on oxidation with nitric acid, the amount obtainable from raffinose should be 22.7 p.c. (Rischbiet and Tollens, *loc. cit.*).

molecule, and further that of R₁₁ and R₁₃ to that of the dextrose and galactose residues in the milk-sugar molecule.

Emil Fischer has proposed the following constitutional formula for milk-sugar—



Schiebler and Mittelmeier consider this to be the most probable formula for melibiose also, but that the difference between the latter and milk-sugar lies in the difference of the combination of the carbinol groups of the dextrose with the aldehyd group of the galactose.

Schiebler and Mittelmeier have found (*Ber.*, xxiii., 1441) that raffinose forms an undecacetyl derivative, C₁₈H₂₁O₅·(OC₂H₃O)₁₁, which is easily soluble in hot alcohol and is precipitated on cooling as an amorphous powder. It melts at 99–100°, has a bitter taste, does not reduce Fehling's solution, and possesses a specific rotation at 17° in 8 per cent. alcoholic solution, [α]_D = 92.2. The existence of this compound indicates that raffinose contains eleven hydroxyl groups, and the presence of a larger number is not conceivable.

THE POISONING OF A FAMILY BY MUSSELS.

By A. B. GRIFFITHS, Ph.D., F.R.S. (Edin.), &c.

ACCORDING to the daily papers "an analysis is being made of the mussels by which Mrs. O'Connor and her four daughters were poisoned at Seapoint, near Dublin, and also of the water where they were gathered. The children had been in the habit of taking mussels from a tidal pond into which the sewage flows, and although it was agreed by the medical men at the inquest that mussels in a healthy state are not poisonous, it was stated that they frequently become so when found in the vicinity of impure water."

There is little doubt that the poisoning was due to the action of alkaloids (ptomaines), developed, by the agency of putrefactive microbes, in the muscular tissues of the mussels in question. Ptomaines belonging to the pyridine and hydropyridine series of organic bases are readily formed when the muscular tissues of the *Invertebrata* (as well as the *Vertebrata*) undergo putrefaction.

Such compounds as:—

Lutidine (C ₇ H ₉ N).	Hydrolutidine (C ₇ H ₁₁ N).
Collidine (C ₈ H ₁₁ N).	Hydrocollidine (C ₈ H ₁₃ N).
Parvoline (C ₉ H ₁₃ N).	—
Coridine (C ₁₀ H ₁₅ N).	Hydrocoridine (C ₁₀ H ₁₇ N).

have been isolated from putrid albuminous substances.

These bases are easily extracted by the methods of Gautier,* Brieger,† and Stas.

Gautier, Brieger, Nencki, Guareschi, Mosso, and the author of this note, have extracted poisonous animal alkaloids belonging to the pyridine and hydropyridine series, as well as certain oxygenised bases, from putrid muscular tissues.

Bearing on the subject of poisoning by mussels, it may be stated that Dr. O. de Coninck (*Comptes Rendus de l'Académie des Sciences*, vol. cvi., p. 858) has recently isolated both collidine and coridine from the muscular tissue of *Sepia officinalis* (the cuttle-fish) after putrefaction.

There is no doubt that pyridine and other bases of a poisonous nature are constant products of the putrefaction

of muscular tissues, not only of the *Vertebrata* but also of the *Invertebrata*.

Hence there is every reason to believe that the poisoning of Mrs. O'Connor and her daughters was due to the formation of poisonous alkaloids by the action of putrefactive microbes on the muscular tissues of the mussels.

FOAM.*

By the Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D.,
F.R.S., Professor of Natural Philosophy, R.I.

(Concluded from p. 4).

I WANT now to bring to your notice certain properties of soap solutions, which, however, are not quite so novel as I thought when I first came upon them in my own inquiries.† If we measure by statical or slow methods the surface tension of soapy water, we find that it is very much less than that of clean water. We can prove this in a very direct manner by means of capillary tubes. Here, shown upon the screen, are two tubes of the same diameter, in which, therefore, if the liquids were the same, there would be the same elevation; one tube dips into clean water, and the other into soapy water, and the clean water rises much (nearly three times) higher than the soapy water.

Although the tension of soapy water is so much less than that of pure water when measured in this way, I had some reason to suspect that the case might be quite different if we measured the tensions immediately after the formation of the surfaces. I was led to think so by pondering on Marangoni's view that the behaviour of foaming liquids was due to the formation of a pellicle upon their surfaces; for if the change of property is due to the formation of a pellicle, it is reasonable to suppose that it will take time, so that if we can make an observation before the surface is more than say $\frac{1}{100}$ of a second old, we may expect to get a different result. That may seem an impossible feat, but there is really no difficulty about it; all that is necessary is to observe a jet of the substance in question issuing from a fine orifice. If such a jet issues from a circular orifice it will be cylindrical at first, and afterwards resolve itself into drops. If, however, the orifice is not circular, but elongated or elliptical, the jet undergoes a remarkable transformation before losing its integrity. As it issues from the elliptical orifice, it is in vibration, and trying to recover the circular form; it does so, but afterwards the inertia tends to carry it over to the other side of equilibrium. The section oscillates between the ellipse in one direction and the ellipse in the perpendicular direction. The jet thus acquires a sort of chain-like appearance, and the period of the movement represented by the distance between corresponding points A, B, Fig. 3, is a measure of the capillary tension to which these vibrations of the elliptical section about the circular form are due. A measure, then, of the wave-length of the recurrent pattern formed by the liquid gives us information as to the tension immediately after escape; and if we wish to compare the tensions of various liquids, all we have to do is to fill a vessel alternately with one liquid and another, and compare the wave-lengths in the various cases. The jet issues from a flask, to which is attached below a tubular prolongation; the aperture is made small in order that we may be able to deal with small quantities of liquid. You now see the jet upon the screen (Fig. 3), it issues from the orifice; it oscillates, and we can get a comparative measure of the tension by observing the distance between corresponding points (A, B).

If we were now to take out the water, and substitute

* *Comptes Rendus*, vol. xciv., p. 1357; p. 1598; vol. xcvi., p. 263; p. 325.

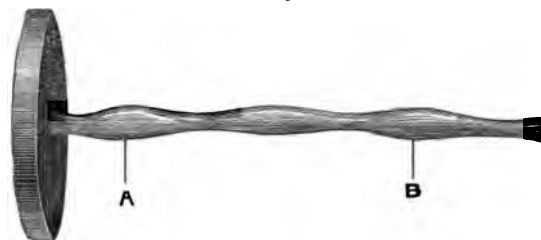
† Über Ptomaines.

* A Lecture delivered at the Royal Institution of Great Britain, March 28, 1890.

† I here allude to the experiments of Dupré, and to the masterly theoretical discussion of liquid films by Professor Willard Gibbs.

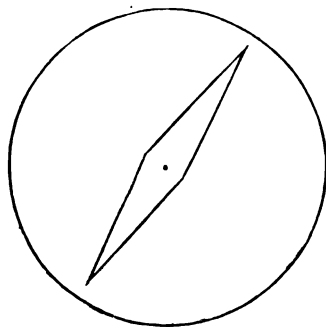
for it a moderately strong solution of soap or saponine, we should find but little difference, showing that in the first moments the tension of soapy water is not very different from that of pure water. It will be more interesting to exhibit a case in which a change occurs. I therefore introduce another liquid, water containing 10 per cent. of alcohol, and you see that the wave-length is different from before. So this method gives us a means of investigating the tensions of surfaces immediately after their formation. If we calculate by known methods how long the surface has been formed before it gets to the point B, at which the measurement is concluded, we shall find that it does not exceed $\frac{1}{100}$ of a second.

FIG. 3.



Another important property of contaminated surfaces is what Plateau and others have described as superficial viscosity. There are cases in which the surfaces of liquids—of distilled water, for example—seem to exhibit a special viscosity, quite distinct from the ordinary interior viscosity, which is the predominant factor in determining the rate of flow through long narrow tubes. Plateau's experiment was to immerse a magnetised compass needle in water; the needle turns, as usual, upon a point, and the water is contained in a cylindrical vessel, not much larger than the free rotation of the needle requires (Fig. 4). The observation relates to the time occupied by the needle in returning to its position of equilibrium in the meridian, after having been deflected into the east and west positions, and Plateau found that

FIG. 4.

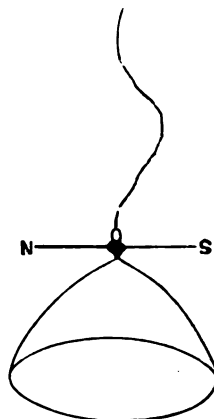


in the case of water more time was required when the needle was just afloat than when it was wholly immersed, whereas in the case of alcohol the time was greater in the interior. The longer time occupied when the needle is upon the surface of water is attributed by Plateau to an excessive superficial viscosity of that body.

Instead of a needle I have here a ring of brass wire (Fig. 5), floating on the surface of the water. You see upon the screen the image of the ring, as well as the surface of the water, which has been made visible by sulphur. The ring is so hung from a silk fibre that it can turn upon itself, remaining all the while upon the surface of the water. Attached to it is a magnetic needle, for the purpose of giving it a definite set, and of rotating it as

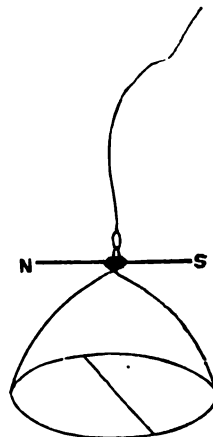
required by an external magnet. On this water, which is tolerably clean, when the ring is made to turn, it leaves the dust in the interior entirely behind. That shows that the water inside the ring offers no resistance to the shearing action brought into play. The part of the surface of water immediately in contact with the ring no doubt goes round; but the movement spreads to a very little distance. The same would be observed if we added soap.

FIG. 5.



But if I add some saponine, we shall find a different result, and that the behaviour of the dust in the interior of the ring is materially altered. The saponine has stiffened the surface, so that the ring turns with more difficulty; and when it turns, it carries round the whole interior with it. The surface has now got a stiffness from which it was free before; but the point upon which I wish to fix your attention is that the surface of pure water does not

FIG. 6.



behave in the same way. If, however, we substitute for the simple hoop another provided with a material diameter (Fig. 6), lying also in the surface of the water, then we shall find, as was found by Plateau in his experiment, that the water is carried round. In this case, it is no longer possible for the surface to be left behind, as it was with the simple hoop, unless it is willing to undergo local expansions and contractions of area. The difference of behaviour proves that what a water surface resists is not shearing, but expansions and contractions; in fact, it behaves just as a contaminated surface should do. On this

supposition, it is easy to explain the effects observed by Plateau; but the question at once arises, can we believe that all water surfaces hitherto experimented upon are sensibly contaminated? and if yes, is there any means by which the contamination may be removed? I cannot in the time at my disposal discuss this question fully, but I may say that I have succeeded in purifying the surface of the water in Plateau's experiment, until it behaved like alcohol. It is therefore certain that Plateau's superficial viscosity is due to contamination, as was conjectured by Marangoni.

I must now return to the subject of foam, from which I may seem to have digressed, though I have not really done so. Why does surface contamination enable a film to exist with greater permanence than it otherwise could? Imagine a vertical soap film. Could the film continue to exist if the tension were equal to all its parts? It is evident that the film could not exist for more than a moment; for the interior part, like the others, is acted on by gravity, and, if no other forces are acting, it will fall 16 feet in a second. If the tension above be the same as below, nothing can prevent the fall. But observation proves that the central parts do not fall, and thus that the tension is not uniform, but greater in the upper parts than in the lower. A film composed of pure liquid can have but a very brief life. But if it is contaminated, there is then a possibility of a different tension at the top and at the bottom, because the tension depends on the degree of contamination. Supposing that at the first moment the film were uniformly contaminated, then the central parts would begin to drop. The first effect would be to concentrate the contamination on the parts underneath and diminish it above. The result of that would be an increase of tension on the upper parts. So the effect would be to call a force into play tending to check the motion, and it is only in virtue of such a force that a film can have durability. The main difference between a material that will foam and one that will not is in the liability of the surface to contamination from the interior.

I find my subject too long for my time, and must ask you to excuse the hasty explanations I have given at some parts. But I was anxious above all to show the principal experiments upon which are based the views that I have been led to entertain.

COLORIMETRIC METHOD FOR ESTIMATING TANNIN IN BARKS, &c.

By SAMUEL J. HINSDALE, Fayetteville, N.C.

DISSOLVE 0.04 grm. potassic ferricyanide in 500 c.c. water, and add to it 1.5 c.c. (about 22 drops) *Liquor Ferri Chloridi*. Call this *Iron Mixture*.

Dissolve 0.04 grm. "Pure Tannin" (gallotannic acid), which has been dried at 212° F. in 500 c.c. of water. Call this *tannin solution*.

Exhaust 0.8 grm. oak bark with boiling water, and make it up to 500 c.c. with cold water.

Place six 2-ounce clear glass tumblers (or beaker glasses) on a white surface, and in one of them, with a dropping pipette (about four inches long and one-quarter inch wide), about half filled, put five drops of the infusion of bark, and in the others, with the same pipette (after rinsing), put 4, 5, 6, 7, and 8 drops of the "tannin solution." (The drops of the infusion and of the tannin solution must be uniform. The use of the same pipette, about half filled, insures that).

Now, add to each 5 c.c. of "iron mixture," and in about one minute add to each tumbler about 20 c.c. water, and within three minutes observe the shades of colour. The number of drops of "tannin solution" used in the tumbler which corresponds in shade of colour to the tumbler containing the infusion of bark indicates the percentage of tannin in the bark, i.e., if it is the one in

which seven drops were placed the tannin strength of the bark is seven per cent.

It is best to observe the shades of colour horizontally rather than vertically, and to hold up the infusion tumbler, with the one which most nearly corresponds, opposite to a white wall, with your back to the light.

The above is written for oak bark, but the same process will answer for any substance containing less than 10 per cent of tannin.

The results are necessarily in terms for commercial gallotannic acid, and not in those of pure tannin or of the particular tannin in the material assayed.

For substances containing between about 10 and 20 per cent, it is best to dilute the infusion with an equal part of water and proceed as above, using five drops of the diluted infusion, and for the answer, double the result. Thus, if the diluted infusion of tea required eight drops tannin solution to correspond, call the percentage sixteen.

For substances containing less than 1, or 1 per cent, exhaust 8 grms. instead of 0.8 grm., and take one-tenth of the result for the answer. For substances containing more than 20 per cent, as galls, sumach, catechu, &c., you may dilute the infusion with two, three, or more times its bulk with water, and calculate as above (as with tea) or you may use 1, 2, 3, or 4 drops of the undiluted infusion in the first glass and make the calculation thus, i.e.:—As the number of drops of infusion used is to the number of drops "tannin solution" used (to correspond), so is 5 to the answer—thus, suppose two drops infusion were used and the corresponding tumbler contained fifteen drops tannin solution—2 : 15 :: 5 ; answer, 37.5 per cent.

The object in diluting the infusions is because the infusion glass may be of too deep a blue shade. It is better that it should just produce a light blue.

The tumblers must be perfectly clear and clean.

The "iron mixture," "tannin solution," and infusion must be freshly prepared and not exposed to the rays of the sun.

The water used must be free of iron and tannin.

THE USE OF NITROSO-β-NAPHTHOL FOR THE DETERMINATION OF IRON AND ITS SEPARATION FROM MANGANESE AND ALUMINIUM.

By L. L. DE KONINCK.

MM. KNORRE and Ilinski have introduced a new reagent, nitroso-β-naphthoquinonoxime. This reagent produces, in certain conditions easily realised, the precipitation of copper, iron, nickel, and cobalt from their saline solutions. Meinecke applies it in the following manner to the determination of iron. The solution free from nitrate, containing the iron as much as possible in the state of ferric chloride or sulphate, is gradually mixed with ammonium carbonate until there is produced a very slight precipitate, which is re-dissolved by one drop of hydrochloric acid. Into the liquid thus obtained there is poured, drop by drop, a solution of nitrosonaphthol in an equal weight of acetic acid at 50 p. c. The quantity of the reagent employed ought to be weighed, so as to have at least 10 parts to 1 part of iron. The precipitate formed is composed of ferric naphtholate mixed with the ferrous salt if the iron is not exclusively in the ferric state, besides the excess of the reagent, which is sparingly soluble in the aqueous liquid. The ferrous naphtholate is more difficult to wash than the ferric salt, whence it is well to peroxidise the iron by bromine by means of bromine or potassium chlorate before proceeding to precipitation. It is known that the precipitation is complete if a drop of the liquid, which has become clear on standing, produces a reddish brown precipitate with a

drop of a cobaltous solution. It is best to operate in the cold to avoid the precipitation of a basic salt of aluminium, and because the precipitate obtained in heat is difficult to wash. It must be washed until the washings leave no fixed residue upon a slip of platinum foil, dried until the contents can be extracted without tearing the filter. It is introduced into a tared porcelain crucible of a sufficient size, folding down the edges of the filter. The crucible is gradually heated, covered with its lid, upon a plate of asbestos until little detonations are no longer produced. The temperature is raised and the residue is ignited uncovered. The product is ferric oxide. Von Knorre advises not to operate upon more than 0.3 gm. The precipitate is not always free from foreign matter. Copper (which is often present in spathic ores in appreciable quantities) and cobalt are carried down, and the phosphoric acid is precipitated either totally or in part. The phosphorus is found entirely in the precipitate if we add ammonium acetate to the neutralised ferric solution before precipitating. The process admits of the separation of iron and manganese, the ferric precipitate being completely free from the latter metal. But the manganic precipitate obtained afterwards by bromine or ammonium sulphide is not more completely free from impurities than if it had been obtained by one of the old methods. It may contain small quantities of silica, nickel, and even iron.

Nitrosonaphthol may be advantageously used for separating iron from aluminium and for determining the latter. According to Von Knorre the separation of iron and aluminium is made by pouring an acetic solution of naphthol at 1-20th into the metallic solution containing a notable excess of acetic acid. Meinecke operates on a solution slightly acid, and with a concentrated solution of the reagent as indicated above. The filtrate from the ferric precipitate is evaporated to expel the excess of acetic acid, and thus prevent the presence of ammonium salts in large proportion. The alumina is then precipitated by ammonia. If much manganese is present it is better to separate the iron and the manganese from other metals by an ordinary process, and to use naphthol only for the respective separation of iron and aluminium.

The presence of the reagent does not interfere with the determination of magnesium and calcium by means of ammonium phosphate and oxalate.—*Revue des Mines* (vol. ix., p. 243).

RECENT SYNTHETICAL EXPERIMENTS IN THE SUGAR SERIES.*

(Concluded from p. 9).

Synthesis of Mannose and Levulose.†

WHEN mannose is oxidised with bromine-water it is converted into mannonic acid. A thorough examination of the properties of mannonic acid showed that it has almost identically the same properties as arabinose-carbonic acid. The latter compound was discovered by Kiliani,‡ and is obtained from the addition-product which is formed by the union of hydrocyanic acid and arabinose. The lactones of these acids are so similar in properties that they would be regarded as identical were it not for the fact that they rotate the plane of polarised light in opposite directions. As their rotatory power is very nearly equal, but in opposite directions, it seemed very probable that they were optical isomers. This supposition proved to be true, for, on mixing solutions of equal weights of the two lactones, an optically inactive compound of the same composition was obtained. This inactive lactone can be transformed into inactive salts and other derivatives, and it is only possible by certain special

methods, to be described below, to again resolve it into its optically active constituents. The three lactones can by reduction be converted into sugars, and these in turn into three hexacid alcohols, and the corresponding members of these three series of reduction-products bear the same relation to each other as do the original lactones. Thus, from the lactone of mannonic acid, mannose and ordinary mannite are obtained, while from the lactone of arabinose-carbonic acid a levo-mannose and a levo-mannite are obtained; and finally, reduction of the inactive lactone gives two corresponding inactive derivatives. The relation of these compounds is shown by Table I.

To avoid confusion, the compounds of the three series are designated by prefixing the letters *d*, *i*, and *l* to their names according to the rotatory power of the sugar of the series. The letter *d* or *l* before the name of a compound does not necessarily imply that the compound is either dextro- or levo-rotatory, but merely that it is a derivative of a dextro- or levo-rotatory sugar. Thus, the two phenylhydrazine derivatives of *d*-mannose are levo-rotatory.

In a recent paper* the preparation and properties of the new sugars *l*-mannose and *i*-mannose and their derivatives are described. Both of them, like *d*-mannose, are stereometric isomers of dextrose. *l*-Mannose can only be fermented with great difficulty, and, like *d*-mannose it is characterised by the insolubility of its hydrazone. *l*-Phenylglucosazone is the optical isomer of ordinary or *d*-phenylglucosazone, and *l*-mannite of ordinary *d*-mannite.

That *i*-mannonic acid is really the optically inactive modification of *d*- and *l*-mannonic acid was shown by splitting it up into its two active components. Two methods were used for this purpose; the first one consisted in subjecting it to fermentation with *Penicillium glaucum*. The *d*-mannonic acid was consumed by the ferment, while the *l*-acid remained behind and was isolated. The second method depended upon the unequal solubility of the strychnine salts of the two acids in absolute alcohol; the salt of the *d*-mannonic acid being much more soluble than the *l* variety, can be readily separated from the latter. A separation of the optically active constituents of *i*-mannose was brought about by fermentation with yeast. When yeast acts upon *i*-mannose, the *d*-mannose is rapidly consumed and the *l*-mannose remains behind.

Perhaps the most important and interesting discovery made in the course of this admirable investigation was the observation that *i*-mannite and α -acrite are identical substances. α -Acrite, it will be remembered, is the hexacid alcohol obtained by the reduction of acrose, the new synthetical sugar which had been built up from glycerin, acrolein bromide, and from formic aldehyd. α -Acrite has identically the same properties that *i*-mannite has, and, like the latter compound, it can be converted into *i*-mannose. α -Acrosazone also is identical with *i*-phenylglucosazone. As, therefore, acrose and *i*-mannose give the same osazone with phenylhydrazine, it follows that the constitution of acrose must be represented by one of the two formulæ:—



i-Mannose.

and—



i-Levulose.

If acrose has the constitution represented by the first one, then it is identical with *i*-mannose, and, like the latter substance, it ought to give a difficultly soluble hydrazone when its solution is treated with phenylhydrazine. Acrose was therefore prepared by direct synthesis from acrolein bromide, and its solution was tested with phenylhydrazine. Under no circumstances

* *American Chemical Journal*, xli., 257.

† *Ber. d. Chem. Ges.*, xxii., 370.

‡ *Ibid.*, xix., 3034.

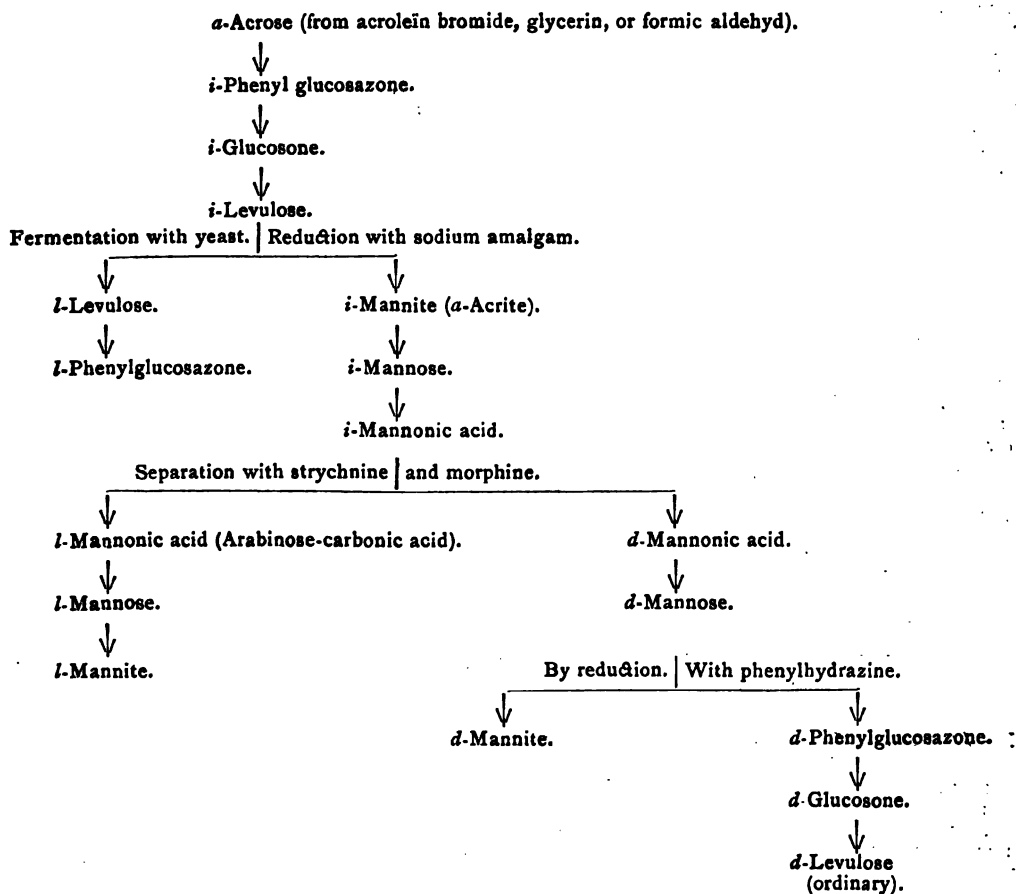
* *Ber. d. Chem. Ges.*, xxiii., 373.

† *Ibid.*, xxiii., 383.

TABLE I,

<i>d-Series.</i>	<i>i-Series.</i>	<i>l-Series.</i>
<i>d</i> -Mannonic acid lactone (dextro-rotatory).	<i>i</i> -Mannonic acid lactone.	<i>l</i> -Arabinose carbonic acid lactone (levo-rotatory).
<i>d</i> -Mannonic acid.	<i>i</i> -Mannonic acid.	<i>l</i> -Arabinose-carbonic acid.
<i>d</i> -Mannose (ordinary) (dextro-rotatory).	<i>i</i> -Mannose.	<i>l</i> -Mannose (levo-rotatory).
<i>d</i> -Mannite (dextro-rotatory).	<i>i</i> -Mannite (α -acrite).	<i>l</i> -Mannite (levo-rotatory).
<i>d</i> -Mannose phenylhydrazone (levo-rotatory).	<i>i</i> -Mannose phenylhydrazone	<i>l</i> -Mannose hydrazone (dextro-rotatory).
<i>d</i> -Phenylglucosazone (levo-rotatory).	<i>i</i> -Phenylglucosazone (α -acrosazone).	<i>l</i> -Phenylglucosazone (dextro-rotatory).

TABLE II.



could the formation of an insoluble hydrazone be observed. This result, therefore, leads to the conclusion that acrose is *i*-levulose, and its constitution must be represented by the second formula. The synthetical sugar obtained from α -acrosazone was also examined in the same way, and, as was to be expected, it also proved to be *i*-levulose.

Further evidence in favour of the view that acrose is

i-levulose was obtained by observing the changes which it undergoes upon fermentation. When acrose was mixed with yeast it was found that one of the optical components, *d*-levulose, was consumed much more rapidly than the other, and after the fermentation had continued for some time, the *l*-levulose was recognised and separated from the solution by means of its osazone. So also the α -acrite, like *i*-mannite, was converted into

i-mannose and *i*-mannonic acid. But the latter compound can be separated into its optically active constituents, and these in turn can be transformed, on the one hand, into *l*-mannose and *l*-mannite, and on the other hand into ordinary mannose and mannite, and into levulose. Thus the complete synthesis of levulose and of the three series of mannite derivatives has been effected. The successive steps in the synthesis are indicated in Table II.

Synthesis of Dextrose.

As has been shown above, *d*-mannose and dextrose have the same constitution and must be regarded as stereometric isomers. Both sugars give the same osazone when treated with phenylhydrazine. It follows, therefore, that the difference between them is due to the asymmetry of the carbon atom as_1 in the formula:—



Fischer also regarded it as highly probable that in mannose the carbon atom as_1 was optically inactive, and that it plays a rôle similar to that of the two carbon atoms in racemic acid. If this supposition is true, then mannonic acid would be related to gluconic acid in the same way that racemic acid is related to one of the active tartaric acids, or this relationship would be analogous to that of racemic acid to mesotartaric acid. In his last paper* Fischer shows that the latter is the true relation. Each of these acids can be transformed into the other. When either one is heated with quinoline to a temperature of 140° , a mixture of the two acids is obtained. This transformation is analogous to that which has been observed in the case of racemic and mesotartaric acids. When either one of these is heated with water to a temperature of 170° — 180° , a mixture of both is obtained.

For the purpose of preparing dextrose, mannonic acid was heated with quinoline, and from the mixture of acids thus obtained the gluconic acid was separated by means of its brucine salt. The brucine salt was decomposed, and the gluconic acid was found to be identical in properties with the gluconic acid obtained by the oxidation of dextrose. The acid was thereupon reduced with sodium amalgam, and from the liquid, *anhydrous crystalline dextrose*, identical in all its properties with ordinary dextrose, was obtained.

The synthesis of dextrose, therefore, is achieved, for, as will be seen in the table printed above, *d*-mannonic acid has been prepared from acrose, and acrose has been made from formic aldehyd.

NOTES ON QUANTITATIVE ANALYSIS.†

By L. H. FRIEDBURG, Ph.D.

(Continued from p. 5).

B.—ANALYSIS OF INSOLUBLE SILICATES, MAINLY PORPHYRIES, &c.‡

A QUANTITY sufficient for eight different assays is crushed, powdered, and sifted through fine muslin. No pressure should be used while dusting, but the muslin which covers a jar and carries the powder is covered by a piece of chamois, and both pieces are tied around the neck of the dry jar. The chamois is then gently tapped with the fingers.

First Portion.

SiO_2 ; Fe; Al; (Mn); Ca; Mg.

The powder is mixed in a platinum crucible with eight times its weight of absolutely dry powdered sodium car-

bonate. The crucible is covered and then heated with the blast lamp. At the beginning of this operation the sleeve at the mouth of the blowpipe is drawn so far forward that an agitated blue flame results. The effect is, that the entire crucible (cover and all) became at once red hot, thus avoiding any decrepitation inside. After a time the sleeve is pushed back, allowing the ordinary flame to play. This is continued for about fifteen minutes, until the mass flows without bubbles. Then the crucible is suddenly cooled by turning off the gas and blowing the cold air from the bellows against it. The cake will subsequently fall out easily, without the necessity of pressing or distorting the crucible. If the fused mass looks merely greenish, this indicates only traces of sodium manganate, but if more intense colouration is visible the presence of manganese must be taken into account in the course of the analysis. The cake is put into a separate beaker containing a little water, the crucible and cover are put into another beaker. Both beakers receive a gradual addition of HCl and are gently heated. After all is dissolved, except gelatinous SiO_2 , the heating is continued until no more CO_2 is present. The combined liquids from the two beakers are then transferred to a platinum dish and evaporated to dryness on the water-bath. The lumps of gelatinous SiO_2 must be frequently crushed so that they cannot enclose soluble silicic acid. The residue is moistened with a few drops of conc. HCl, then diluted with water, and filtered with the pump. The filter with SiO_2 is (after complete washing) put while moist into a platinum crucible, heated, and weighed until the weight is constant. The silicic acid is then treated with HF (free from all residue), and a few drops of H_2SO_4 upon the water-bath, until all volatile matter is driven off; the residual H_2SO_4 is expelled over a free flame; the residue, if any, is heated to redness and weighed. The treatment with HF and H_2SO_4 may be repeated if necessary. In case the residue should be considerable it must be quantitatively tested for Al, Fe, Ca, and Mg, otherwise a qualitative test is sufficient.

The filtrate from the SiO_2 determination is heated and oxidised by a few drops of HNO_3 , after which Fe and Al are precipitated with a very slight excess of NH_4OH , and the unavoidable excess of this latter is boiled off immediately. Care should be taken not to expose this liquid too long to the air. It would attract CO_2 and precipitate Ca. If an interruption is unavoidable, the beaker must be placed upon a dish containing a layer of NH_4OH and a larger beaker must be inverted over the smaller one, its edge immersed in the layer. The precipitate consists of Fe_2O_3 and Al_2O_3 , with small traces of SiO_2 , Ca, and Mg.

This precipitate may be treated in two different ways, according as it is smaller or larger, especially as regards the quantity of iron present.

1. *For Small Quantities of Iron.*—The precipitate is heated and weighed, then fluxed with potassium bisulphate in a closed crucible at low temperature, so as just to make the mass flow, cooled, dissolved in water; the iron is reduced with zinc and the solution titrated with permanganate. In case HCl was used to dissolve the reduced iron, H_2SO_4 is added before titration, in excess, because the sulphate solution is lighter in colour than the chloride, and also because strong dilution is desirable.

2. *The Precipitate is abundant, and much Iron is present.*—Dissolve in HCl and digest for half an hour in a platinum dish with an excess of KOH upon the water-bath. The details of manipulation are as follows:—The precipitate being washed thoroughly, is, for the greatest part, brought into the platinum dish by means of a platinum spatula. The remaining portions on the filter are dissolved in a hot mixture of equal parts of conc. HCl and H_2O by means of a pipette. The solution is allowed to run into the main precipitate in the platinum dish. The filter is washed with water; this filtrate running into a beaker. The mass in the platinum dish is then cautiously treated with KOH solution, a few pieces of solid KOH

* *Ber. d. Chem. Ges.*, xxiii, 799.

† From the *Journal of the American Chemical Society*, vol., xii, No. 5.

‡ This process, with few changes, was commonly used in Bunsen's laboratory.—L. H. F.

are added, digestion for half an hour upon the water-bath follows, and the mass is then diluted with the wash filtrate which was collected separately in the beaker and filtered through the aforesaid filter. This filtrate contains the Al_2O_3 . Acidulate with HCl , so that solution just takes place after the first precipitation, and precipitate with freshly prepared ammonium sulphide. This latter is used in preference to ammonium hydrate, because Al_2O_3 is less soluble in the former; the $(\text{NH}_4)_2\text{S}$ must be freshly prepared in order to avoid polythionic salts, as well as ammonia resulting from decomposition by age.

The previously mentioned precipitate containing Fe_2O_3 (and traces of CaO , MgO , and SiO_2) is heated and weighed. Of course, the crucible during this heating must remain open, in order to avoid reduction by gases from the flame. Dissolve in conc. HCl , filter from SiO_2 , re-precipitate iron with NH_4OH , and add the filtrate to the liquid containing these substances. SiO_2 and Fe_2O_3 are to be treated as described before, and weighed separately.

Should the remaining filtrate now be too abundant it must be concentrated after acidulation with HCl . A little NH_4OH is added to precipitate remaining Al_2O_3 , and, if this is still present, the ammonia is driven off and the precipitate filtered, added to the first precipitate, heated, and weighed as Al_2O_3 .

The combined filtrates, concentrated as above, contain Mn , Ca , and Mg for determination. If enough Mn were present this must first be precipitated by means of ammonium sulphide. Wash with water containing some $(\text{NH}_4)_2\text{S}$, re-dissolve in HCl , boil the solution to separate sulphur, and filter. Concentrate the filtrate, precipitate with Na_2CO_3 , boil in order to destroy manganese carbonate which might have formed, wash with boiling water, heat, and weigh as Mn_2O_4 .

Before precipitating Ca , the filtrate must be acidulated with HCl , thus separating sulphur, and then filtered. Render slightly alkaline with NH_4OH and add ammonium oxalate, boiling. Filter after twelve hours. Put the moist well-washed filter, with precipitate, into a platinum crucible, heat strongly for fifteen minutes before the blast lamp, and weigh as CaO . This weight must be controlled. Re-dissolve the CaO in HCl , re-precipitate as above, and add the filtrate to the liquid containing Mg . Heat the CaO to constancy before the blast-lamp. Test it with the spectroscope for Ba and Sr .

Before precipitating Mg (particularly if this is present in small quantity only) drive off the ammonium salt as thoroughly as possible. Dissolve in a little HCl until the liquid is slightly acid, add sodium phosphate, then ammonium hydrate until a turbidity sets in, then a quantity of ammonium hydrate equal to one-third of the volume of the liquid: filter after four hours and wash with a mixture of one part of NH_4OH and three parts of water. Formerly, a period of twenty-four hours was deemed necessary for this precipitation, but, generally, four hours are fully sufficient. The precipitate is washed until no more chlorine is present. Now, either dry the filter with precipitate and incinerate separately, or, better, especially if the pump was used for washing, bring the moist precipitate and filter into a platinum crucible. Heat gently at first, finally before the blast lamp energetically. Should the pyrophosphate prove to contain a little carbon, moisten with a few drops of HNO_3 , evaporate cautiously to dryness, and heat again, as above.

If the spectroscopic research proved the presence of sufficient Ba and Sr , the CaO precipitate has to be further treated. Transfer from the platinum crucible into a small thin well tempered flask of 5 to 10 c.c. capacity. Wash the residue from the crucible with HNO_3 into the flask, and add more HNO_3 to this latter, until all Ca is transformed into nitrate. The solution may be turbid from filter ash or from Ba or Sr salts. Evaporate over a small direct flame to dryness, blow out the residual HNO_3 vapour by means of a glass pipe, and add not more alcohol than is necessary to obtain, on heating, a syrupy

solution of calcium nitrate. Allow to stand for twenty-four hours, filter from barium and strontium nitrate, wash with absolute alcohol. If a sufficient quantity now remains upon the filter, dissolve this in hot water and allow the solution to run into a weighed platinum crucible. Evaporate to dryness and heat before the blast to constant weight (BaO and SrO). Now dissolve in conc. HCl , evaporate in the same little flask as previously used to dryness, separate SrCl_2 , soluble in absolute alcohol by means of this. Precipitate BaCl_2 as sulphate, and weigh. Sr is found by difference. In case no weighable amount of BaCl_2 should have remained after the SrCl_2 was dissolved in absolute alcohol, allow the syrup of SrCl_2 to be taken up by a strip of filter-paper, wind around this a thin platinum wire, incinerate in an open flame, heat until the sodium flame has disappeared, and then use the spectroscope, dipping the platinum wire frequently into HCl . Mere traces of Ba will only become visible after almost perfect evaporation of SrCl_2 .

Second Portion.

Determination of the Alkalies.

The powder is put into a platinum crucible, moistened with a few drops of conc. H_2SO_4 and then digested three or four times with conc. HF upon the water-bath. This done, the small crucible is put upright inside of and near the bottom of a large platinum crucible lying horizontally. A small flame is applied underneath the side nearest the mouth of the large crucible and the burner is gradually pushed towards the middle and near the end. The H_2SO_4 and hydrofluosilicic acid are thus expelled. This expulsion must be performed thoroughly, so that afterwards no glass vessel may be attacked by remaining HF . The small platinum crucible is not allowed to become red hot in order that alkalies may not be lost. Should the mineral not have been fully decomposed, the resulting mass must again be treated with HF on the water-bath and afterwards heated, as described. Now, while the large crucible is put vertically and the small one inserted into the same, enough conc. HCl is added to dissolve all CaSO_4 , and the large crucible containing the small one standing within is heated upon the water-bath. Generally it is found that a residue is left. The liquid must then be decanted and the residue treated as before. After perfect solution the contents of the small crucible are emptied into the large one, washing carefully. Then BaCl_2 and (without filtering) NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ are added and the precipitate is filtered and washed and the united filtrates are evaporated to dryness. The ammonia salts are expelled by very cautious heating, so that no decrepitation may take place. The residue is dissolved in water, NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ are again added, filtration, evaporation, and expulsion of ammonia salts is repeated again and again, until no further precipitate is formed by addition of these reagents. It is advisable to use for every new filtration a smaller platinum dish, so as not to get too much filtrate. The final solution must be absolutely free from ammonium salts.

A small quantity of pure, red HgO is added in order to transform MgCl_2 into MgO while HgO is transformed into volatile HgCl_2 . The platinum dish is covered with a watch-glass and digested (so that the mass is just kept moist) for two hours. An excess of water has to be avoided, or else the reaction does not take. After this dry for 1 to 2 hours on the water-bath, and finally drive off the HgCl_2 by heating, but not to redness. Dissolve in a minimum of water, filter into a weighed platinum crucible, add a drop of HCl , evaporate to dryness, heat so as to keep the mass just in a fused state in the covered crucible, and then weigh. In order to obtain thus the sum of the alkaline chlorides, this heating and weighing has to be repeated to constancy. After the first weighings a new addition of HCl is advisable, since (owing to organic substances from the filter) carbonates may have formed in heating.

Now dissolve in a few drops of water and add an excess of platinic chloride. (The preparation of c.p. platinic chloride will be given at the end of this chapter). Care has to be taken that all NaCl is transformed into the double salt; no white cubes must remain visible in the precipitate, since these would be insoluble in alcohol. Evaporate to dryness on the water-bath and in a *porcelain* dish. This is easily understood. In the first place the mixed chlorides of alkalis are generally dissolved and filtered after weighing, since an unavoidable residue of Fe may be present, which must be considered; secondly, the platinic chloride must not be evaporated in a platinum dish, as it would dissolve platinum as subchloride, which is insoluble in alcohol, and would result together with potassium-platinic chloride. Allow to cool, add a few drops of water in order to dissolve the sodium double salt, and throw on a filter previously washed with alcohol, dried at 105° C. and weighed. Then wash the potassium double salt first with a mixture of 1 part alcohol and 1 part water, then with 1 part water and 2 parts alcohol, finally with absolute alcohol until the filtrate runs colourless. Then wash with a mixture of 4 parts alcohol and 1 part ether. The filtrates must be preserved for the following reason: In case the determination of MgO in the filtrate should not be necessary, but that the precipitate of K_2PtCl_6 should be lost, the $PtCl_4$ would have to be reduced to metallic platinum, as described below, in order to obtain NaCl.

The precipitate is dried at 105° C. and weighed to constancy.

The filtrate is diluted with water, heated to drive off ether and alcohol, and then put into a little flask with doubly perforated stopper, which carries two rectangular bent tubes. One of these latter nearly reaches the surface of the liquid, the other ends in the neck of the flask. This second one is connected with a hydrogen apparatus. The flask is heated gently, and, while still hot, the longer rectangular tube is closed outside by means of a rubber tube with glass rod. The hydrogen apparatus is now set to work, the flask cools, and the hydrogen absorbed by reduction is thus replaced spontaneously. The liquid becomes colourless and platinum is dendritically separated, generally floating for some time upon the liquid, which is now filtered. If some FeO should still be present, a drop of HNO_3 is added and then NH_4OH . The precipitate, if any, is filtered. Then MgO is determined and deducted as $MgCl_2$ from the above found sum of the combined alkaline chlorides.

Preparation of C. P. Platinic Chloride.

The platinic chloride used in the above determination is prepared, according to Bunsen, in the following manner, which involves the separation of platinum from iridium, rhodium, and palladium:—

Dissolve platinum in aqua regia, taking 4 pts. HCl and 1 pt. HNO_3 , adding this latter very gradually while the flask stands on the water-bath. After complete solution has taken place evaporate, also on the water-bath, to a syrup, add water and evaporate again as before, repeating this process until upon renewed addition of a drop of water to the syrup no odour of nitrous acid is perceptible.

Now dissolve in water and filter into a porcelain dish. Add sodium hydrate solution, until strongly alkaline, while the liquid is kept boiling, and continue to boil after the addition for a few seconds, during which time a drop or two of alcohol are added. At first the oxides of all the metals are thus formed, but after a while the excess of NaOH transforms Ir, Rh, and Pd into the sesquioxides, while platinum remains as oxide. Sodium hypochlorite is formed at the same time, but this is destroyed by the addition of a little alcohol.

If now HCl be added and the heating continued a yellow precipitate is first formed, while the HCl and the excess of NaOH have just neutralised each other. Heating is continued, and more HCl is added until the yellow precipitate is re-dissolved.

Platinic chloride and the sesquichlorides of Ir, Pd, and Rh are formed.

All of these are soluble, but only the platinic chloride is precipitated by potassium chloride. To the clear filtrate is added a hot saturated solution of KCl, until no more precipitate is formed. After cooling, the canary yellow precipitate of K_2PtCl_6 is filtered, washed with a solution of KCl, saturated in the cold, dried very thoroughly, and reduced in a long, absolutely dry Bohemian glass tube by means of hydrogen at a very low temperature. The tube is put in an ordinary combustion furnace and the flames are kept very low.

After all of the double salt has become uniformly black, the mass is allowed to cool in the hydrogen current. The contents of the tube are then transferred to a porcelain dish, boiled with water and decanted, or filtered by decantation. This boiling is repeated until all KCl is dissolved and the wash water does not show the chlorine reaction. The pure platinum obtained is now dissolved in aqua regia, as described above for the impure metal, and the syrup is treated with water until no further escape of nitrous acid takes place.

Third Portion.

Hygroscopic Water.—Heat the substance (powdered as described), at 105° C. to constant weight. **Water of Combination.**—Heat the material for 15–20 minutes to redness in a Bohemian bulb tube and collect H_2O in a weighed $CaCl_2$ tube. Allow to cool in a current of cold dried air. In case the silicate should contain FeO, the heating has to be performed in a current of CO_2 , since it is desirable to weigh the bulb tube also for control.

Fourth Portion.

Take a well dried Bohemian glass tube, 1 foot long, closed at one end, and put into it, by means of a long weighing tube, about 1 grm. of substance. With the aid of a long capillary funnel tube moisten the mass uniformly with some drops of water. Prepare a mixture of 6 pts. conc. H_2SO_4 and 2 pts. H_2O , allow it to cool, and pour it through the same funnel tube upon the substance, until it occupies 8 to 10 times the volume of the latter. Reduce the diameter of the tube greatly at about 2 inches from its open end and replace the air above the liquid with carbon dioxide. Seal before the blast lamp. After cooling, shake the tube vigorously in order to avoid caking. Heat the sealed tube for 4 to 5 hours in a thermostat at 200° or 220° C. When quite cold open the tube, transfer its contents, without filtering, into a high beaker, wash rapidly, and titrate with permanganate solution, the titre of which has been determined immediately before use. It is evident that in presence of organic matter in the silicate this determination cannot be performed.

(To be continued).

Pyridin and its Relations to Quinoline, Isoquinoline, and the Alkaloids.—Alb. Edinger.—The author concludes that a pyridin of Dewar's formula *might* exist, but does not exist in a free state and uncontaminated with an isomer.—*Journal für Praktische Chemie*, xli., Part 7.

Behaviour of Silica and its Compounds in Microcosmic Salt.—J. Hirschwald.—Small admixtures of silica cannot be determined by means of this reagent, as it dissolves in not inconsiderable quantities in the bead of the double salt. In many cases silicates may indeed be detected in the manner in question (1) by the characteristic corrosive perforations of the sample used in the form of a splinter, and (2) by its relative insolubility in comparison with other compounds. It has, however, no decisive analytical importance, as many minerals free from silica (e.g. wavellite, monazite, apatite, diaspor, &c.), behave in the same manner as the silicates.—*Journal für Praktische Chemie*, xli., Part 7.

CORRESPONDENCE.

ELECTROLYTIC ASSAY OF COPPER.

To the Editor of the Chemical News.

SIR,—In assaying copper by the electrolytic process I frequently find the deposited copper at the beginning of the process to be of a dark brown colour, and when this is so the remainder of the copper comes down fluffly, and as I have no time to investigate the matter can you give me an explanation as to what the deposit consists of, and what will prevent its occurrence? The copper is always separated by HS_2 before precipitating as metal.—I am, &c.,

DEPOSIT.

ESTIMATION OF ALUMINA IN IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—In answer to Mr. C. H. Ridsdale's letter (CHEMICAL NEWS, vol. lxii., p. 11), I beg to state that my method for the estimation of aluminium in iron and steel published in the CHEMICAL NEWS (vol. lxi., p. 313) is, in reality, a combination of other methods, carefully thought out and put together. I do not, therefore, claim originality for it; and, though Mr. Stead may have had his method in print first, I must say that the method has been worked by me in the estimation of aluminium in ferro-aluminium alloys for a number of years, and have used the same method for the determination of aluminium in steel for the past seven months, not having been called upon before to execute the same, and I certainly had no idea that Mr. Stead had been working on the same lines, as his method did not come to my hand until the receipt, in May, of the second part of vol. iv. of the *Journal of Analytical Chemistry*. I have since then tried his method, and have found that it takes nearly double the time of execution, this being a consideration; therefore I think Mr. Ridsdale cannot claim all the credit of priority for Mr. Stead.—I am, &c.,

CHARLES PHILLIPS.

Chemical and Metallurgical Laboratories,
8, Market Street, Fitzalan Square,
Sheffield, July 7, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 25, June 23, 1890.

The Reciprocal Action of the Alkaline and Mercurous Haloid Salts.—A. Ditté.—The decomposition of mercurous chloride by sodium chloride into soluble mercurial salt and metallic mercury is only a special case of a general action exerted by the alkaline haloid salts upon the mercurous haloid salts, and which is effected in two different manners, the action being in some cases exothermic and in others endothermic.

Certain Lithium, Glucinum, Lead, and Uranium Phosphates.—L. Ouvrard.—The author has sought to obtain simple and double phosphates by dissolving the metallic oxides or carbonates in melted alkaline phosphates. He has obtained tribasic lithium phosphate, and he remarks that lithium deviates from the other members of the alkaline group by the insolubility of its phosphate. Glucinum gives, with potassium meta-pyro- or orthophosphates only a single salt, $\text{PO}_3, 2\text{BeO}, \text{KO}$, which

forms, with sodium metaphosphate, a double salt, agreeing in composition with the mineral beryllonite. With lead the author obtains a product similar in its composition to the glucinum salt, and forming a double sodium salt. Melting potassium metaphosphate yields, with uranium sesquioxide, a pyrophosphate in which uranyl oxide plays the part of a protoxide.

Combinations of Double Phosphorus and Iridium Chlorides with Arsenic Chloride.—G. Geisenheimer.—The double iridium and phosphorus chloride described in the *Comptes Rendus* (May 12, 1890) dissolves readily in arsenic chloride. The compound dissolves in water with liberation of hydrochloric acid.

Silver Subfluoride.—M. Gunz.—This compound contains 91.86 per cent of silver and 8.14 per cent of fluorine. It is unalterable in dry air, and is only slowly decomposed in moist air.

A Contribution to the Study of the Ptomaines.—Oechsner de Koninck.—This communication relates to the ptomaine $\text{C}_{10}\text{H}_{15}\text{N}$. When in a state of purity it is a slightly yellowish viscid liquid, of a pleasant odour, slightly soluble in water, very soluble in ether, absolute alcohol, acetone, and in the light ligroines. Its sp. gr. is about = 1.18, and it boils about 230° . It is very quickly oxidised in presence of atmospheric oxygen, turning brown and depositing a thick resin, soluble in acids. It does not attract carbon dioxide from the atmosphere. The hydrochlorate, $\text{C}_{10}\text{H}_{15}\text{N} \cdot \text{HCl}$, is prepared by rapidly saturating the ptomaine with HCl and evaporating *in vacuo*. If an exceedingly minute quantity of air is allowed to enter under the bell the salt instantly takes a rose colour, and in presence of a larger quantity of air it turns red and then brown. The chloroplatinate is a deep red powder, insoluble in cold water, very soluble in hot water, but decomposed in boiling water.

Preparation of the Yeasts of Wine.—A. Rommèr.—For obtaining the wine-yeasts the author uses grapes, the seeds of which he selects, crushes, and introduces them into small flasks. Several specimens were prepared in order to have at least one exempt from bacteria and mycoderms. When fermentation has set in the flasks are gently agitated, and one or two drops of the liquid were let fall into other flasks containing grape-juice rendered clear by filtration and sterilised by heat. On microscopic examination some of the samples were at once rejected. At last only the yeast was left, known as *Saccharomyces ellipsoideus*.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. ix., Nos. 2 and 3.

The Production and Decomposition of Carbonic Acid in Coke-Blast Furnaces.—Felix Brabant.—The author considers that his results prove the possibility of improving the working of many furnaces, notwithstanding the persistence of a loss resulting from a reduction of CO_2 to CO .

Studies on the Processes for the Analysis of Raw Materials and Finished Products in the Metallurgy of Iron.—C. Meinecke.

Determination of Phosphorus by Molybdenum.—The question is raised whether the presence of manganese interferes with the precipitation? The author answers in the negative, and suspects that the results of M. Tamm must be due to his having operated upon spiegel and ferro-manganese without calcining the nitrates. He asks with what certainty may we conclude from the proportion of phosphorus directly precipitable by molybdate in the nitric solution of an iron as to the total phosphorus present? He admits that the proportion of phosphorus immediately precipitable by molybdate after the solution of the sample in nitric acid is liable to great variation. These may probably be made to disappear by operating always under identical conditions.

Oxidation of the Solution by Chromic Anhydride or Permanganate.—The author, Mr. Wood, has recommended oxidation by chromic acid to obtain the totality of phosphorus in a form precipitable by molybdate without evaporating down the nitric solution and calcining the residue. The author recommends the use of a sufficiency of nitric acid (avoiding excess), and by an addition of sulphuric acid. The details of this process, and of the use of nitroso- β -naphthol for the determination of iron and its separation from manganese and aluminium, are inserted in full. (See p. 19).

Vol. x., Nos. 1 and 2.

Corrosions of Steam-Boilers and the Incrustations in Marine Boilers.—The author, M. Schwarz, Inspector of Steam-Boilers in Austria, divides the corrosive agents into four groups:—(1) Gases held in solution by the feed-water; (2) insoluble matter; (3) soluble matter; and (4) volatile acids. The gases in question are chiefly oxygen and carbonic acids. The remedy is their elimination by a previous heating to 70°, or by rendering the water alkaline by a small addition of soda. The insoluble matters are animal and vegetable fats employed in lubrication. Corrosion may be prevented by the use of sodium carbonate, and the use of mineral oils in lubrication is a certain preservative. The soluble injurious matters are either such whose action increases with temperature and concentration, and comprise sodium chloride, ammonium chloride introduced by certain anti-incrustation nostrums, and caustic soda in the Honigmann boilers. The free acids are nitric acid in the waste waters of zinc works, organic acids in the waters from marshy lands, hydrochloric and sulphuric acid from the waste waters of bleach works, and sulphuric acid from the waters of mines and quarries. Corrosion by these agents is prevented by means of soda. Among the substances whose corrosive action begins at a higher temperature are the brown liquor from wood in the chemical preparation of cellulose, saccharine liquors in sugar works, and magnesium chloride. The general means for preventing the damage consists in the addition of a little soda, and sometimes in the introduction of plates of zinc.

Journal für Praktische Chemie.

New Series, Vol. xli., Nos. 4, 5, and 6.

Researches from the Laboratory of A. Weddige.—A paper on alkyl-ortho-phenyldiamines and its derivatives. Alkyl-ortho-phenyldiamines in an acid solution pass into alkylimido-benzols by the action of sodium nitrite. On the action of the same nitrite upon acetyl-orthophenyldiamine hydrochlorates, or by passing nitrous gas into the ethereal solution, there is no production of nitrosoacetylalkylorthophenyldiamines. Nitronitroso-alkylanilines are obtained by treating orthonitroalkylanilines with nitrous gas. These nitroso-compounds in acid solutions are not converted by reducing agents into the corresponding hydrazines, but into alkylortho-phenyldiamines. In alcoholic solutions they can be converted into orthoamidophenylalkylhydrazines by ammonium sulphide. Acetorthoamidophenylmethylhydrazine can be converted into α -phenyltriazine by appropriate treatment with phosphoric anhydride. On treating orthoamidophenylalkylhydrazines with sodium nitrite in an acid solution there are formed α -alkylphenyltriazines.

A New Method for the Preparation of Aromatic Mercaptans.—R. Leuckhart. Aniline and its homologues have been converted into phenylmercaptan and the homologous aromatic mercaptans. Ortho- and para-amidophenol were transformed into monothiopyrocatechin and monothiohydroquinone, &c. The conversions were in general obtained most smoothly about 70°, the diazo-compounds obtained at lower temperatures are often decomposed explosively on a rise of temperature.

The Action of Iodoform, Methyleniodide, and Iodine upon Sodium Isobutylate.—A. Gorbhoff and A. Kessler.—This memoir does not admit of useful abstraction.

Monazite from the Ural.—C. W. Blomstrand.—From the analyses it appears that we cannot, with Penfield, allot thoria exclusively to silicic acid, since, in most cases, the cerium and yttrium earths do not suffice to saturate the phosphoric acid.

Researches from the Laboratory of Prof. Saytseff at Kasan.—These consist of a paper by S. Reformatsky on the first oxide of the quadrivalent alcohols.

Researches from the Laboratory of the University of Freiburg.—These include memoirs on dichloronaphthoquinone dichloride, by Ad. Claus, and on the special arrangement of the atoms in nitrogenous compounds, by C. Willgerodt.

MISCELLANEOUS

The Diseases of Crops.—Messrs. George Bell and Sons will publish in a few days an octavo volume entitled "The Diseases of Crops and their Remedies," by Dr. A. B. Griffiths, F.R.S.E. The work is illustrated with 51 figures, and the chemical treatment of plant diseases is fully discussed.

The Behaviour of Ammonium Formiate upon Ketones.—R. Leuckart.—It results from these researches that ammonium formiate, in its behaviour with acetone, acts like free ammonia, and has, at the same time, a reducing effect. That the course of the transformation is here quite different from that in the simple aldehyds and ketones of the aromatic series depends on the peculiar nature of the ketones of the aliphatic series.—*Journal für Praktische Chemie*, xli., Part 7.

TO CORRESPONDENTS.

T. Smyth.—The annual subscription to the Chemical Society is £2 2s., with £2 2s. entrance fee. A letter to the Secretary of the Society, Burlington House, London, W., will get you all necessary information.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that the BADISCHE ANILIN AND SODA FABRIK, of Ludwigshafen-on-Rhine, in the Empire of Germany, have applied for leave to amend the Specification of Letters Patent No. 15,259 of 1888, granted to James Yate Johnson for "The manufacture of the sulpho-acids of a red basic naphthalene dye-stuff."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on the 2nd July, 1890.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed)

H. READER LACK,
Comptroller-General.

J. H. JOHNSON AND CO.,
47, Lincoln's Inn Fields, London, W.C.,
Agents for the Badische Anilin and
Soda Fabrik.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that

HENRY HARRINGTON LEIGH, of 22, Southampton Buildings, London, W.C., has applied for leave to amend the Specification filed in pursuance of the application for Letters Patent No. 1300 of 1890, for "Improvements in the manufacture of anhydrous barium oxide."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on the 2nd July, 1890.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed)

H. READER LACK,
Comptroller-General.

THE CHEMICAL NEWS.

VOL. LXII. No. 1599.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

THE substances alluded to in this paper may be divided into three distinct classes according to their behaviour with sulphur chloride. The solid magma which some of them yield with this reagent may be either totally soluble in carbon disulphide or only partially soluble, whilst others simply act as solvents, and apparently undergo no change. This reaction enables us to separate one class of these substances from the other two.

Assuming that we have taken every precaution to obtain a representative sample as regards purity, age, and condition of the substance operated on, we have the advantage of securing a product which can easily be kept for reference or comparison, a matter of no small importance when we consider how liable most oils are to change in a short time.

Many of the oils referred to have been prepared by myself where the sources were available, or from manufacturers of repute in cases where I have had to depend on others for the integrity of a sample.

Oils and fats obtained from animal sources, fish oils, and the concrete vegetable oils do not yield insoluble products, but are easily separated from the fluid vegetable oils, when a mixture of them is acted on by sulphur chloride. Oils obtained from pine resins behave in a similar way. The fluid vegetable oils, when deprived of a portion of their glycerin, behave in the same way, as regards their altered portion.

Hence, if a rapid stream of oxygen or ozonised oxygen (by preference) be passed through a mixture of these oils, the more easily oxidised oil can be separated from those not so readily acted on. The fatty acids of these oils do not form insoluble compounds, and are recognised by yielding dark coloured products.

Olive oil adulterated with cotton-seed oil and lard oil can easily be recognised by this treatment. Lard oil can be washed out by carbon disulphide from the solid magma; another portion well oxidised will, by the same solvent, give up both the lard oil and the fatty acids of the cotton-seed oil. The insoluble magma will be very dark, owing to the difficulty of entirely removing the oxidised oil. Treatment with a moderately strong alkaline solution will more effectually remove it. I have frequently met with a mixture of these oils having an iodine absorption closely approaching that of pure olive oil.

When pure olive oil is acted upon for some time with ozonised oxygen the colour of the insoluble product, reveals the fact that little or no absorption has taken place, pure olive oil is probably the most stable of all the vegetable oils, hence its non-suitability as a "drying oil."

Drying oils or the more easily oxidised oils, such as poppy oils, seed oil, walnut oil, linseed oil, rape, and cotton-seed oils are readily recognised. When either of these oils or a mixture containing either of them is ozonised, a reduced factor for iodine absorption is at once apparent; the extent or rapidity of oxidation is measured by the rate of diminution of iodine absorption.

A so-called "cold drawn oil" has a higher iodine absorption than when heat is used, and when the oil has been extracted from the seeds by solvents a still higher iodine absorption is noticeable. This is due in a great measure to oxidation, which reduces the iodine absorption in proportion to the extent to which it is carried.

From a consideration of this fact, it is easy to conceive that olive oil will vary according to the condition of the olive when pressed. In the plant economy the assimilation of oxygen in the ripening of the fruit would lead one to say that a reduced iodine absorption should follow. Experiment, however, does not confirm this assumption, which will be referred to hereafter.

Cotton-seed oil, as such, is rarely used for adulterations; in some cases the olein and in other cases the stearin, both more or less impure, are used.

Lard oil, which is used as a lubricant, contains, very frequently, a large proportion of cotton oil stearin, whereas oleomargarin contains principally cotton oil olein.

Machine oils containing *thickened* or *blown* oils of cotton seed or rape seed, so as to obtain an increased viscosity, are easily recognised. The viscosity of an oil before and after passing oxygen through it is an important indication in the analysis of oils; a drying oil is detected by an alteration in the iodine absorption and increased viscosity.

Iodine Absorption of Oils, &c.—Anyone who has worked on this subject must have found that comparable results involve most scrupulous care in every detail connected with its application.

Hubl's Reagent.—When a great number of samples have to be examined a litre of this reagent may be made, but, as it rapidly alters it should not be kept longer than a week or so. When only a few samples have to be dealt with, a waste from deterioration and other causes can hardly be avoided unless the samples are allowed to accumulate, which is undesirable, even if delay involves no inconvenience.

The solutions of mercuric chloride and iodine, separately, will keep tolerably well for some time, but, if mixed together, continue to change every day. This difficulty is met by making the alcoholic solutions of proper strength and mixing them as required; in this way a single sample of oil may be examined without waste or extra trouble. When little or nothing is known of a sample the test should be made in duplicate to guard against accident in the final titration with sodium thiosulphate. A blank test on the same quantity of Hubl chloroform employed should always be made, the mixture standing for the same time and in the same place as the oil under test. The reaction is allowed to go on in a dark cupboard, which is supplied with a registering thermometer so as to record the changes of temperature during the time. An accurately stoppered yellow tinted flask is used, about 6 ozs. capacity, the flasks and stoppers being marked so as to avoid being changed. The upper part of the neck is enlarged so as to admit of being luted with a little potassium iodide solution, to catch any iodine which may escape between the neck and stopper. An accurately fitting glass cap encloses the stopper and lute.

When the reaction is allowed to go on for four or six hours, as recommended, an awkward difficulty arises, due partly to the fact that it is not always possible to attend to the final titration at the precise time, and what is of more importance, an hour's extra digestion will make a very great difference in the result. To avoid the chance of this occurring, the reaction is allowed to go on for twenty to twenty-four hours, as I have found that after eighteen hours no appreciable change occurs, a matter of importance in a general laboratory. The test can be put on and finished towards the end of each day.* Volatile liquids are weighed in a stoppered flask or measured from an accurate pipette.

It is generally assumed that all oils have the same coefficient of expansion. From some recent experiments on the capacity for heat of different oils I found that oils

* A paper recently read by Messrs. Thomson and Ballantyne before the Society of Chemical Industry on the "Revision of Oil Constants" confirms the liability of absorption to alter with increased digestion.

vary considerably in their expansions, but care must be taken to conduct such experiments, so as to avoid ingress of atmospherical oxygen or loss of volatile products.

When oils are sent out by a manufacturer the casks are filled nearly to the bung; if a slight increase of temperature takes place the expansion forces the oil through any weak places in the package and into the wood itself; hence a serious loss must fall to the lot of the buyer; with olive or sperm oil the loss is more serious, as these oils become more fluid and do not dry up.

DETERMINATION OF PHOSPHORUS IN IRON.

In order to obtain the whole of the phosphorus in a state precipitable by molybdate without evaporating down the nitric solution and igniting the residue, Herr Meinecke and Mr. Wood recommend oxidation with chromic acid. They dissolve 4.375 grms. of the metal in a covered vessel in 40 to 50 c.c. of nitric acid at sp. gr. 1.3 (if the iron is very manganiferous 40 c.c. are sufficient). When the solution is completed 30 c.c. of dilute sulphuric acid are added (1 vol. acid to 1 vol. water), and the liquid is evaporated down to 15–20 c.c. From 2½ to 3 grms. chromic acid in crystals (not more) are then added, and the liquid is boiled for ten minutes to complete the oxidation of the carbon compounds and of the phosphorous acid. It is let partly cool and water is carefully added. If the evaporation has been carried too far, manganese peroxide may separate out and retain phosphorus; if this happens the peroxide must be reduced by the addition of oxygenated water. It must be remembered that all samples of oxygenated water met with in commerce contain phosphoric acid in small quantities. Hence if much of this reagent has to be used account must be taken of this impurity.

The solution contains, in an insoluble state, only a little graphite and silica; it is made up to 250 c.c., filtered through a dry filter, and 100 c.c. are taken by means of a pipette. The acid is partially neutralised by means of ammonia, heated to 85°–90°, and 50 to 100 c.c. of the molybdic reagent are added. It is convenient to precipitate in a vessel so large that it may be only half full. In this case, by leaning the beaker after the precipitate is settled we may uncover a part of the bottom. If we then cautiously bring back the beaker to its normal position that part of the bottom remains free from deposit. If, after the lapse of half an hour, we find that no fresh deposit is formed, we know that the precipitation is completed, and we then draw off the clear supernatant liquid by means of a small syphon.

The precipitate is collected on a filter as small as possible, washed at first with an acid solution of ammonium nitrate, then with pure water, and is lastly transformed into molybdenum phosphomolybdate, $P_2O_5Mo_{24}O_{68}$, by a moderate ignition. Each gm. of the product corresponds to one per cent of phosphorus.

M. von Reiss in the analysis of steels uses potassium permanganate instead of chromic acid and obtains satisfactory results.

The author has used the same process, slightly modified, with success in the analysis of cast metal rich in carbon.

He dissolves 4.375 grms. of the metal in 40 c.c. of nitric acid. If the sample is rich in manganese there is obtained on the addition of permanganate an immediate precipitate of peroxide. The results are always satisfactory on operating as follows:—To the nitric solution of the metal there are added 25 c.c. of nitric acid at sp. gr. 1.4; then 5 c.c. permanganate at 15 per thousand and the liquid is boiled. After a few minutes a fresh portion of permanganate is added, and then a third under the same conditions. There is then produced a manganic precipitate, which a new and final addition of permanganate increases. The liquid is then boiled for a few

minutes longer, cooled quickly, and the oxide is removed by oxygenated water added in small successive proportions. The liquid contains all the phosphorus in the state of a phosphate precipitable by molybdate.—*Revue des Mines*, ix., p. 239.

THE PHOTOGRAPHIC IMAGE.*

By Professor RAPHAEL MELDOLA, F.R.S.

THE history of a discovery which has been developed to such a remarkable degree of perfection as photography has naturally been a fruitful source of discussion among those who interest themselves in tracing the progress of science. It is only my presence in this lecture theatre, in which the first public discourse on photography was given by Thomas Wedgwood at the beginning of the century, that justifies my treading once again a path which has already been so thoroughly well beaten. If any further justification for trespassing upon the ground of the historian is needed, it will be found in the circumstance that in the autumn of last year there was held a celebration of what was generally regarded as the jubilee of the discovery. This celebration was considered by many to have reference to the public disclosure of the Daguerreotype process, made through the mouth of Arago to the French Academy of Sciences on August 10, 1839. There is no doubt that the introduction of this process marked a distinct epoch in the history of the art, and gave a great impetus to its subsequent development. But, while giving full recognition to the value of the discovery of Daguerre, we must not allow the work of his predecessors and contemporaries in the same field to sink into oblivion. After the lapse of half a century we are in a better position to consider fairly the influence of the work of different investigators upon modern photographic processes.

I have not the least desire on the present occasion to raise the ghosts of dead controversies. In fact, the history of the discovery of photography is one of those subjects which can be dealt with in various ways, according to the meaning assigned to the term. There is ample scope for the display of what Mr. Herbert Spencer calls the "bias of patriotism." If the word "photography" be interpreted literally as writing or inscribing by light, without any reference to the subsequent permanence of the inscription, then the person who first intentionally caused a design to be imprinted by light upon a photosensitive compound must be regarded as the first photographer. According to Dr. Eder, of Vienna, we must place this experiment to the credit of Johann Heinrich Schulze, the son of a German tailor, who was born in the Duchy of Magdeburg, in Prussia, in 1687, and who died in 1744, after a life of extraordinary activity as a linguist, theologian, physician, and philosopher. In the year 1727, when experimenting on the subject of phosphorescence, Schulze observed that by pouring nitric acid, in which some silver had previously been dissolved, on to chalk, the undissolved earthy residue had acquired the property of darkening on exposure to light. This effect was shown to be due to light, and not to heat. By pasting words cut out in paper on the side of the bottle containing his precipitate, Schulze obtained copies of the letters on the silvered chalk. The German philosopher certainly produced what might be called a temporary photogram. Whatever value is attached to this observation in the development of modern photography, it must be conceded that a considerable advance was made by spreading the sensitive compound over a surface instead of using it in mass. It is hardly necessary to remind you here that such an advance was made by Wedgwood and

* A Lecture delivered at the Royal Institution of Great Britain, May 16, 1890.

Davy in 1802.* The impressions produced by these last experimenters were, unfortunately, of no more permanence than those obtained by Schulze three quarters of a century before them.

It will, perhaps, be safer for the historian of this art to restrict the term photograph to such impressions as are possessed of permanence: I do not, of course, mean absolute permanence, but ordinary durability in the common-sense acceptance of the term. From this point of view, the first real photographs, *i.e.*, permanent impressions of the camera picture, were obtained on bitumen films by Joseph Nicéphore Niepce, of Châlons-sur-Saône, who, after about twenty years' work at the subject, had perfected his discovery by 1826. Then came the days of silver salts again, when Daguerre, who commenced work in 1824, entered into a partnership with Niepce in 1829, which was brought to a termination by the death of the latter in 1833. The partnership was renewed between Daguerre and Niepce de St. Victor, nephew of the elder Niepce. The method of fixing the camera picture on a film of silver iodide on a silvered copper plate—the process justly associated with the name of Daguerre, was ripe for disclosure by 1838, and was actually made known in 1839.

The impartial historian of photography who examines critically into the evidence will find that, quite independently of the French pioneers, experiments on the use of silver salts had been going on in this country, and photographs, in the true sense, had been produced almost simultaneously with the announcement of the Daguerreotype process, by two Englishmen whose names are as household words in the ranks of science—I refer to William Henry Fox Talbot and Sir John Herschel. Fox Talbot commenced experimenting with silver salts on paper in 1834, and the following year he succeeded in imprinting the camera picture on paper coated with the chloride. In January, 1839, some of his "photogenic drawings"—the first "silver prints" ever obtained—were exhibited in this Institution by Michael Faraday. In the same month he communicated his first paper on a photographic process to the Royal Society, and in the following month he read a second paper before the same society, giving the method of preparing the sensitive paper and of fixing the prints. The outcome of this work was the "Calotype" or Talbotype process, which was sufficiently perfected for portraiture by 1840, and which was fully described in a paper communicated to the Royal Society in 1841. The following year Fox Talbot received the Rumford Medal for his "discoveries and improvements in photography."†

Herschel's process consisted in coating a glass plate with silver chloride by subsidence. The details of the method, from Herschel's own notes, have been published by his son, Prof. Alexander Herschel.‡ By this means the old 40-foot telescope at Slough was photographed in 1839. By the kindness of Prof. Herschel, and with the sanction of the Science and Art Department, Herschel's original photographs have been sent here for your inspection. The process of coating a plate by allowing a precipitate to settle on it in a uniform film is, however, impracticable, and was not further developed by its illustrious discoverer. We must credit him, however, as being the first to use glass as a substratum. Herschel further discovered the important fact that while the chloride was very insensitive alone, its sensitiveness was greatly increased by washing it with a solution of silver nitrate. It is to Herschel, also, that we are indebted for the use of sodium thiosulphate as a fixing agent, as well as for many other discoveries in connection with photography, which are common matters of history.

* "An Account of a Method of Copying Paintings upon Glass, and making Profiles by the Agency of Light upon Nitrate of Silver. Invented by T. Wedgwood, Esq. With Observations by H. Davy," *Journ. R. I.*, 1802, p. 170.

† For these and other details relating to Fox Talbot's work, necessarily excluded for want of time, I am indebted to his son, Mr. C. H. Talbot, of Lacock Abbey.

‡ *Photog. Journ. and Trans. Photog. Soc.*, June 15, 1872.

Admitting the impracticability of the method of subsidence for producing a sensitive film, it is interesting to trace the subsequent development of the processes inaugurated about the year 1839. The first of photographic methods—the bitumen process of Niepce—survives at the present time, and is the basis of some of the most important of modern photo-mechanical printing processes. [Specimens illustrating photo-etching from Messrs. Waterlow and Sons exhibited.] The Daguerreotype process is now obsolete. As it left the hands of its inventor it was unsuited for portraiture, on account of the long exposure required. It is evident, moreover, that a picture on an opaque metallic plate is incapable of reproduction by printing through, so that in this respect the Talbotype possessed distinct advantages. This is one of the most important points in Fox Talbot's contributions to photography. He was the first to produce a transparent paper negative from which any number of positives could be obtained by printing through. The silver print of modern times is the lineal descendant of the Talbotype print. After forty years' use of glass as a substratum, we are going back to Fox Talbot's plan, and using thin flexible films—not exactly of paper, but of an allied substance, celluloid. [Specimens of Talbotypes, lent by Mr. Crookes, exhibited, with celluloid negatives by the Eastman Company.]

If I interpret this fragment of history correctly, the founders of the modern photography are the three men whose labours have been briefly sketched. The jubilee of last autumn marked a culminating point in the work of Niepce and Daguerre, and of Fox Talbot. The names of these three pioneers must go down to posterity as co-equal in the annals of scientific discovery. [Portraits by Mr. H. M. Elder shown.] The lecture theatre of the Royal Institution offers such tempting opportunities to the chronicler of the history of this wonderful art that I must close this treatment of the subject by reminding myself that in selecting the present topic I had in view a statement of the case of modern photography from its scientific side only. There is hardly any invention associated with the present century which has rendered more splendid services in every department of science. The physicist and chemist, the astronomer and geographer, the physiologist, pathologist, and anthropologist will all bear witness to the value of photography. The very first scientific application of Wedgwood's process was made here by the illustrious Thomas Young, when he impressed Newton's rings on paper moistened with silver nitrate, as described in his Bakerian Lecture to the Royal Society on November 24, 1803. Prof. Dewar has just placed in my hands the identical slide, with the Newton rings still visible, which he believes Young to have used in this classic experiment. [Shown.]

Our modern photographic processes depend upon chemical changes wrought by light on films of certain sensitive compounds. Bitumen, under this influence, becomes insoluble in hydrocarbon oils, as in the heliographic process of the elder Niepce. Gelatin mixed with potassium dichromate becomes insoluble in water on exposure to light, a property utilised in the photo-etching process introduced in 1852 by Fox Talbot, some of whose original etchings have been placed at my disposal by Mr. Crookes. [Shown.] Chromatised gelatin now plays a most important part in the autotype and many photo-mechanical processes. The salts of iron in the ferric condition undergo reduction to the ferrous state under the influence of light in contact with oxidisable organic compounds. The use of these iron salts is another of Sir John Herschel's contributions to photography (1842), the modern "blue print" and the beautiful platinotype being dependent on the photo-reducibility of these compounds. [Cyanotype print developed with ferricyanide.]

Of all the substances known to chemistry at the present time, the salts of silver are by far the most important in photography, on account of the extraordinary degree of sensitiveness to which they can be raised. The photo-

graphic image, with which it is my privilege to deal on this occasion, is that invisible impression produced by the action of light on a film of a silver haloid. Many methods of producing such films have been in practical use since the foundation of the art in 1839. All these depend on the double decomposition between a soluble chloride, bromide, or iodide, and silver nitrate, resulting in the formation of the silver haloid in a vehicle of some kind, such as albumen (Niepce de St. Victor, 1848), or collodion on glass, as made practicable by Scott Archer in 1851. For twenty years this collodion process was in universal use; its history and details of manipulation, its development into a dry plate process by Colonel Russell in 1861, and into an emulsion process by Bolton and Sayce in 1864, are facts familiar to every one.

The photographic film of the present time is a gelatino-haloid (generally bromide) emulsion. If a solution of silver nitrate is added to a solution of potassium bromide and the mixture well shaken, the silver bromide coagulates, and rapidly subsides to the bottom of the liquid as a dense curdy precipitate. [Shown.] If instead of water we use a viscid medium, such as gelatin solution, the bromide does not settle down, but forms an emulsion, which becomes quite homogeneous on agitation. [Shown.] This operation, omitting all details of ripening, washing, &c., as well known to practical photographers, is the basis of all the recent photographic methods of obtaining negatives in a camera. The use of this invaluable vehicle, gelatin, was practically introduced by R. L. Maddox in 1871, previous experiments in the same direction having been made by Gaudin (1853-61). Such a gelatino-bromide emulsion can be spread uniformly over any substratum—glass, paper, gelatin, or celluloid—and when dry, gives a highly sensitive film.

The fundamental problem which fifty years' experience with silver haloid films has left in the hands of chemists is that of the nature of the chemical change which occurs when a ray of light falls on such a silver salt. Long before the days of photography—far back in the sixteenth century—Fabricius, the alchemist, noticed that native horn silver became coloured when brought from the mine and exposed. The fact presented itself to Robert Boyle in the seventeenth century, and to Beccarius, of Turin, in the eighteenth century. The change of colour undergone by the chloride was first shown to be associated with chemical decomposition in 1777, by Scheele, who proved that chlorine was given off when this salt darkened under water. I can show you this in a form which admits of its being seen by all. [Potassium iodide and starch paper were placed in a glass cell with silver chloride, and the arrangement exposed to the electric light till the paper had become blue.] The gas which is given off under these circumstances is either the free halogen or an oxide, or acid of the halogen, according to the quantity of moisture present and the intensity of the light. I have found that the bromide affects the iodide and starch paper in the same way, but silver iodide does not give off any gas which colours the test paper. All the silver haloids become coloured on exposure to light, the change being most marked in the chloride, less in the bromide, and least of all in the iodide. The latter must be associated with some halogen absorbent to render the change visible. [Strips of paper coated with the pure haloids, the lower halves brushed over with silver nitrate solution, were exposed.] The different degrees of colouration in the three cases must not be considered as a measure of the relative sensitiveness: it simply means that the products of photo-chemical change in the three haloids are inherently possessed of different depths of colour.

From the fact that halogen in some form is given off, it follows that we are concerned with photo-chemical decomposition, and not with a physical change only. All the evidence is in favour of this view. Halogen absorbents, such as silver nitrate on the lower halves of the papers in the last experiment, organic matter, such as the gelatin in an emulsion, and reducing agents generally, all

accelerate the change of colour. Oxidising and halogenising agents, such as mercuric chloride, potassium dichromate, &c., all retard the colour change. [Silver chloride paper, painted with stripes of solutions of sodium sulphite, mercuric chloride, and potassium dichromate, was exposed.] It is impossible to account for the action of these chemical agents except on the view of chemical decomposition. The ray of light falling upon a silver haloid must be regarded as doing chemical work; the vibratory energy is partly spent in doing the work of chemical separation, and the light passes through a film of such haloid partly robbed of its power of doing similar work upon a second film. It is difficult to demonstrate this satisfactorily in the lecture-room, on account of the opacity of the silver haloids, but the work of Sir John Herschel, J. W. Draper, and others, has put it beyond doubt that there is a relationship of this kind between absorption and decomposition. It is well known, also, that the more refrangible rays are the most active in promoting the decomposition in the case of the silver haloids. This was first proved for the chloride by Scheele, and is now known to be true for the other haloids. It would be presumption on my part, in the presence of Captain Abney, to enlarge upon the effects of the different spectral colours on these haloids, as this is a subject upon which he can speak with the authority of an investigator. It only remains to add that the old idea of a special "actinic" force at the more refrangible end of the spectrum has long been abandoned. It is only because the silver haloids absorb these particular rays that the blue end of the spectrum is most active in promoting their decomposition. Many other instances of photo-chemical decomposition are known in which the less refrangible rays are the most active, and it is possible to modify the silver haloids themselves, so as to make them sensitive for the red end of the spectrum.

The chemical nature of the coloured products of photo-chemical decomposition is still enshrouded in mystery. Beyond the fact that they contain less halogen than the normal salt, we are not much in advance of the knowledge bequeathed to us by Scheele in the last century. The problem has been attacked by chemists again and again, but its solution presents extraordinary difficulties. These products are never formed—even under the most favourable conditions of division and with prolonged periods of exposure—in quantities beyond what the chemists would call "a mere trace." Their existence appears to be determined by the great excess of unaltered haloid with which they are combined. Were I to give free rein to the imagination, I might set up the hypothesis that the element silver is really a compound body invariably containing a minute percentage of some other element, which resembles the compound which we now call silver in all its chemical reactions, but alone is sensitive to light. I offer this suggestion for the consideration of the speculative chemist.* For the coloured product as a whole, i.e., the product of photo-decomposition with its combined unchanged haloid, Carey Lea has proposed the convenient term "photo-salt." It will avoid circumlocution if we adopt this name. The photo-salts have been thought at various times to contain metallic silver, allotropic silver, a sub-haloid, such as argentous chloride, &c., or an oxyhaloid. The free metal theory is disposed of by the fact that silver chloride darkens under nitric acid of sufficient strength to dissolve the metal freely. The acid certainly retards the formation of the photo-salt, but does not prevent it altogether.

* I have gone so far as to test this idea experimentally in a preliminary way, the result being, as might have been anticipated, negative. Silver chloride, well darkened by long exposure, was extracted with a hot saturated solution of potassium chloride, and the dissolved portion, after precipitation by water, compared with the ordinary chloride by exposure to light. Not the slightest difference was observable either in the rate of colouration or in the colours of the products. Perhaps it may be thought worth while to repeat the experiment, using a method analogous to the "method of fractionation" of Crookes.

When once formed the photo-chloride is but slowly attacked by boiling dilute nitric acid, and from the dry photo-salt mercury extracts no silver. The assumption of the existence of an allotropic form of silver insoluble in nitric acid cannot be seriously maintained. The subhaloid theory of the product may be true, but it has not yet been established with that precision which the chemist has a right to demand. We must have analyses giving not only the percentage of halogen, but also the percentage of silver, in order that it may be ascertained whether the photo-salt contains anything besides metal and halogen. The same may be said of the oxyhaloid theory: it may be true, but it has not been demonstrated.

The oxyhaloid theory was first suggested by Robert Hunt* for the chloride; it was taken up by Sahler, and has recently been revived by Dr. W. R. Hodgkinson. It has been thought that this theory is disposed of by the fact that the chloride darkens under liquids, such as hydrocarbons, which are free from oxygen. I have been repeating some of these experiments with various liquids, using every possible precaution to exclude oxygen and moisture; dry silver chloride, heated to incipient fusion, has been sealed up in tubes of dry benzene, petroleum, and carbon tetrachloride, and exposed since March. [Tubes shown.] In all cases the chloride has darkened. The salt darkens, moreover, in a Crookesian vacuum.† By these experiments the oxychloride theory may be scotched, but it is not yet killed; the question now presents itself, whether the composition of the photo-salt may not vary according to the medium in which it is generated. Analogy sanctions the supposition that when the haloid darkens under water or other oxygen-containing liquid, or even in contact with moist or dry air, that an oxychloride may be formed, and enter into the composition of the photo-salt. The analogy is supplied by the corresponding salt of copper, viz., cuprous chloride, which darkens rapidly on exposure. [Design printed on flat cell filled with cuprous chloride by exposure to electric light.] Wöhler conjectured that the darkened product was an oxychloride, and this view receives a certain amount of indirect support from these tubes [shown], in which dry cuprous chloride has been sealed up in benzene and carbon tetrachloride since March; and although exposed in a southern window during the whole of that time, the salt is as white as when first prepared. Some cuprous chloride sealed up in water, and exposed for the same time, is now almost black. [Shown.]

When silver is precipitated by reduction in a finely divided state in the presence of the haloid, and the product treated with acids, the excess of silver is removed and coloured products are left which are somewhat analogous to the photo-salts proper. These coloured haloids are also termed, by Carey Lea, photo salts, because they present many analogies with the coloured products of photo-chemical change. Whether they are identical in composition it is not yet possible to decide, as we have no complete analyses. The first observations in this direction were published more than thirty years ago in a report by a British Association Committee;‡ in

which the red and chocolate-coloured chlorides are distinctly described. Carey Lea has since contributed largely to our knowledge of these coloured haloids, and has at least made it appear highly probable that they are related to the products formed by the action of light. [Red photo-chloride and purple photo-bromide and iodide shown.]

The photographic image is impressed on a modern film in an inappreciable fraction of a second, whereas the photo-salt requires an appreciable time for its production. The image is invisible simply because of the extremely minute quantity of haloid decomposed. In the present state of knowledge it cannot be asserted that the material composing this image is identical in composition with the photo-salt; for we know the composition of neither the one nor the other. But they are analogous in so far as they are both the result of photo-chemical decomposition, and there is great probability that they are closely related, if not identical, chemically. It may turn out that there are various kinds of invisible images, according to the vehicle or halogen absorbent—in other words, according to the sensitiser with which the silver haloid is associated. The invisible image is revealed by the action of the developer, into the function of which I do not propose to enter. It will suffice to say that the final result of the developing solution is to magnify the deposit of photo-salt by accumulating metallic silver thereon by accretion or reduction. Owing to the circumstance that the image is impressed with such remarkable rapidity, and that it is invisible when formed, it has been maintained, and is still held by many, that the first action of light on the film is molecular or physical, and not chemical. The arguments in favour of the chemical theory appear to me to be tolerably conclusive, and I will venture to submit a few of them.

The action of reagents upon the photographic film is quite similar to the action of the same reagents upon the silver haloids when exposed to the point of visible colouration. Reducing agents and halogen absorbents increase the sensitiveness of the film; oxidising and halogenising agents destroy its sensitiveness. It is difficult to see on the physical theory why it should not be possible to impress an image on a film, say, of pure silver bromide, as readily as on a film of the same haloid embedded in gelatin. Everyone knows that this cannot be done. I have myself been surprised at the extreme insensitiveness of films of pure bromide prepared by exposing films of silver deposited on glass to the action of bromine vapour. On the chemical theory we know that gelatin is a splendid sensitiser—i.e., bromine absorbent. There is another proof which has been in our hands for nearly thirty years, but I do not think it has been viewed in this light before. It has been shown by Carey Lee, Eder, and especially by Abney—who has investigated the matter most thoroughly—that a shearing stress applied mechanically to a sensitive film leaves an impression which can be developed in just the same way as though it had been produced by the action of light. [Pressure marks on Eastman bromide paper developed by ferrous oxalate.] Now that result cannot be produced on a surface of the pure haloid, some halogen absorbent, such as gelatin, must be associated with the haloid. We are concerned here with a chemical change of that class so ably investigated by Prof. Spring, of Liège, who has shown that by mere mechanical pressure it is possible to bring about chemical reaction between mixtures of finely-divided solids.* Then, again, mild reducing agents, too feeble to

* "Researches on Light," and Ed., 1854, p. 80.

† Some dry silver chloride which Mr. Crookes has been good enough to send up for me in a high vacuum, darkens on exposure quite as rapidly as the dry salt in air. It soon regains its original colour when kept in the dark. It behaves, in fact, just as the chloride is known to behave when sealed up in chlorine, although its colour is of course much more intense after exposure than is the case with the chloride in chlorine. The tube in which the chloride had been sealed up in benzene gave off a considerable quantity of hydrogen chloride on breaking the point in June.

‡ These results were arrived at in three ways. In one case hydrogen was passed through silver citrate suspended in hot water, and the product extracted with citric acid. "The result of treating the residue with chlorhydric acid, and then dissolving the silver by dilute nitric acid, was a rose-tinted chloride of silver." In another experiment the dry citrate was heated in a stream of hydrogen at 212° F., and the product, which was partly soluble in water, gave a brown residue, which furnished "a very pale red body on being transformed by chlorhydric and nitric acids." In another experiment silver arsenite was formed, this being treated with caustic soda, and the black precipitate then treated successively with chlorhydric and

nitric acids: "Silver is dissolved, and there is left a substance . . . [of] a rich chocolate or maroon, &c." This on analysis was found to contain 24 per cent of chlorine, the normal chloride requiring 24.7, and the sub-chloride 14.08 per cent. The committee which conducted these experiments consisted of Messrs. Maskelyne, Hadow, Hardwich, and Llewellyn. "B. A. Rep." 1859, p. 103.

* The connection between the two phenomena was suggested during a course of lectures delivered by me two years ago ("Chemistry of Photography," p. 191). I have since learnt that the same conclusion had been arrived at independently by Mr. C. H. Bothamley, of the Yorkshire College, Leeds.

reduce the silver haloids directly to the metallic state, such as alkaline hypophosphites, glucose or lactose, and alkali, &c., form invisible images which can be developed in precisely the same way as the photographic image. All this looks like chemical change, and not physical modification pure and simple.

I have in this discourse stoically resisted the tempting opportunities for pictorial display which the subject affords. My aim has been to summarise the position in which we find ourselves with respect to the invisible image after fifty years' practice of the art. This image is, I venture to think, the property of the chemist, and by him must the scientific foundation of photography be laid. We may not be able to give the formula of the photo-salt, but if the solution of the problem has hitherto eluded our grasp it is because of the intrinsic difficulties of the investigation. The photographic image brings us face to face—not with an ordinary, but with an extraordinary class of chemical changes due entirely to the peculiar character of the silver salts. The material composing the image is not of that definite nature with which modern chemical methods are in the habit of dealing. The stability of the photo-salt is determined by some kind of combination between the sub-haloid or oxy-haloid, or whatever it may be, and the excess of unaltered haloid which enters into its composition. The formation of the coloured product presents certain analogies with the formation of a saturated solution; the product of photo-chemical decomposition is formed under the influence of light up to a certain percentage of the whole photo-salt, beyond which it cannot be increased—in other words, the silver haloid is saturated by a very minute percentage of its own product of photo-decomposition. The photo-salt belongs to a domain of chemistry—a no-man's land—peopled by so-called "molecular compounds," into which the pure chemist ventures but timidly. But these compounds are more and more urging their claims for consideration, and sooner or later they will have to be reckoned with, even if they lack that definiteness which the modern chemist regards as the essential criterion of chemical individuality. The investigation may lead to the recognition of a new order of chemical attraction, or of the old chemical attraction in a different degree. The chemist who discourses here upon this subject at the end of the half-century of photography into which we have now entered, will no doubt know more about this aspect of chemical affinity; and, if I may invoke the spirit of prophecy in concluding, I should say that a study of the photographic film with its invisible image will have contributed materially to its advancement.

NOTES ON QUANTITATIVE ANALYSIS.*

By L. H. FRIEDBURG, Ph.D.

(Concluded from p. 24).

Fifth Portion.

For the determination of phosphoric acid fuse with Na_2CO_3 as directed for first portion, but dissolve in HNO_3 instead of using HCl . Reduce the silicic acid to a sandy powder, filter and acidulate with nitric acid. Prepare a solution of ammonium molybdate in the following manner: 100 grms. molybdic acid suspended in 240 grms. distilled water, of a temperature of about 50°C . are mixed with 160 grms. of NH_4OH of sp. gr. 0.91. If necessary, filter and allow this solution to run gradually into 1250 c.c. HNO_3 of sp. gr. 1.20. Shake at intervals and allow the clear solution to rest for five or six days in a moderately warm, dark place. Decant or syphon, if necessary, from yellow precipitate, and add H_2O to make 2 litres. Preserve this reagent in the dark.

In case the amount of phosphoric acid in the sample does not amount to more than one decigramme, and provided the volume of the liquid to be tested does not exceed 150 c.c., add an excess of the above solution of ammonium molybdate and put the beaker into a water-bath containing boiling water. Allow the beaker to remain for ten minutes in the boiling water and all phosphoric acid will be precipitated.

If the mineral is richer in phosphoric acid it must be treated with an excess of ammonium molybdate in a warm place for fully twenty-four hours.

In either case the precipitate is filtered, washed at first with the molybdate solution used for precipitation, finally with a solution of one-third that strength, obtained by dilution with H_2O . The united filtrates are allowed to stand for a while in order to see if an additional precipitate is formed.

The yellow precipitate on the filter is quantitatively dissolved in NH_4OH .

Magnesium mixture is now prepared in the following manner:—Magnesium chloride is dissolved in conc. HCl in the proportion of 5 grms. MgCl_2 to 30 c.c. HCl . Dilute with water and supersaturate with strong NH_4OH . If the liquid should not remain clear, but precipitate magnesia, enough NH_4Cl must be added to re-dissolve this.

Of a solution thus prepared, take a certain volume and divide into halves. One half is added to the ammoniacal solution of phospho-ammonium molybdate, after this has been nearly neutralised with HCl . Finally add strong NH_4OH , amounting to one-third of the entire volume of the liquid. Allow this to stand three to four hours.

Fill up the other half of the magnesium mixture taken, with the same quantity of NH_4OH used in forming the precipitate just described, and then with H_2O to obtain the same volume. A precipitate of magnesia formed here should be deducted from the previously described one.

The filtration, washing, and heating until magnesium pyrophosphate is obtained, takes place according to the description given, I.

Sixth Portion.

Fluorine is quite frequently found in silicates containing phosphoric acid. To determine F fuse the silicate, duly prepared, with Na_2CO_3 as previously described. Boil the cake with H_2O and a little NH_4OH in order to expel CO_2 , thus preventing solution of either SiO_2 or alumina. Filter, add HCl until the liquid is almost neutral. (Avoid acidity, since HF might escape.) Digest for some time with NH_4Cl in order to separate all SiO_2 and Al_2O_3 , filter if necessary, add CaCl_2 solution, and filter the precipitate consisting of calcium fluoride, calcium phosphate, and calcium carbonate. Heat the precipitate to redness in a porcelain crucible. Now, after cooling, add acetic acid and evaporate the mass again to dryness. Continue this treatment with acetic acid, alternating with washing with water and decanting, until the weight of the residue remains constant. In this manner calcium acetate and phosphate are extracted and calcium fluoride remains.

Seventh Portion.

In order to determine titanate, the mineral is fused with potassium bisulphate, using six to eight times the quantity of this latter. Dissolve the fused mass in a little cold water, dilute strongly, and boil slowly in a round flask. From time to time add water, since titanate acid is only precipitated from very dilute solutions. In order to prevent precipitate of Fe add either sulphur dioxide, sodium hyposulphite, or H_2S to the liquid, thus reducing Fe_2O_3 or avoiding the oxidation of FeO . The precipitate of titanate acid is heated and weighed. If not quite colourless repeat the operation.

Eighth Portion.

For the determination of soluble silicic acid treat the mineral in a platinum crucible with conc. KOH solution upon the water-bath for one-quarter to one-half hour.

* From the *Journal of the American Chemical Society*, vol. xii., No. 5.

Avoid too great concentration of the liquid, as the silicic acid dissolved would be re-precipitated. If it be suspected that the mineral decomposes, heat only for a short time. The contents of the crucible are transferred to a beaker, diluted strongly, washed by decantation with boiling water until no further reaction of KOH is obtained. The residue is heated and weighed; the operation is repeated until the weight is constant.

If, upon decantation, the precipitate should not settle or should run turbid through the filter, a slight acidulation of the wash water will frequently serve. In case free quartz was present, this would become partly soluble on heating. In such case the mineral is treated several times with KOH solution, decanted each time as described, but only heated and weighed once, which weight must then suffice.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act, 1871.*

London, July 5th, 1890.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, the whole were found to be clear, bright, and well filtered.

The character of the water supply to the Metropolis during the month of June has not exhibited any features calling for special remark. As usual, the proportion of organic matter, inconsiderable, save on exceptional occasions, even at its highest, is somewhat higher in the case of the Thames-derived water than in the case of that derived wholly or in large part from the Lea. Taking the water furnished by the Companies deriving their supply from the Thames for comparison, the mean proportion of organic carbon was found to be 0.150 part in 100,000 parts of the water, with a maximum of 0.166 part in any single sample examined.

During the past six months of the year we have examined a total of 1455 samples of the Metropolitan water supply. Speaking generally, the water has been characterised to a more than usually noticeable degree, by its uniformity of composition from month to month. Thus, taking the Thames-derived samples for comparison, the mean proportion of organic carbon for the six months' period was found to be 0.150 part in 100,000 parts of the water, or identical with the mean proportion for the present month; while in five samples only was the proportion found to reach or exceed 0.170 part, the maximum in any

single sample examined being 0.174 part in 100,000 parts of the water.

Similar conclusions are afforded generally by a comparison of the numbers expressing the amounts of oxygen consumed, and degrees of freedom from colour-tint of the successive monthly supplies. It is to be noted, however, that while the curves representing the variations noted by the three several methods of examination, show a marked correspondence when the variations are, relatively speaking, at all considerable, their correspondence, as might be expected, is of a less strict or more general character only, in the case of such inconsiderable variations as have alone had to be recorded during the past six months.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

ON THE ELECTRO-DEPOSITION OF PLATINUM.*

By W. H. WAHL.

THE permanence and unalterability of the metal platinum—properties which make it of such inestimable value to the chemist—have likewise suggested its application as a protective covering upon the surfaces of other metals; and, even in the early days of the art of electro-deposition, efforts to obtain a satisfactory coating of this metal were made. The failure with which these early experiments were attended served rather to stimulate than to deter subsequent investigators, and the problem has received the attention of a number of the most noted experts in the art. The results that have been accomplished cannot be said to have been entirely satisfactory—a statement which, I believe, will be fully sustained by the fact that electro-plating with platinum, on the commercial scale, is practised only to a very limited extent. When the wide field of application for platinum-plating is considered—and I need only name philosophical, engineering, surgical, dental and electrical apparatus and instruments, fire-arms, watch-cases, and jewellery, to say nothing of the host of miscellaneous articles of utility and ornament to which the metal could be advantageously applied—the conclusion is irresistible, that the processes thus far proposed for the purpose do not fully meet the requirements of practical service.

Thus far, of all the methods that have been proposed for electro-plating with platinum, three only appear to have sufficient merit to deserve special notice; these are:—

(1) Roseleur-Lanaux method, based on the electrolysis of a solution of the double phosphate of sodium and platinum.

(2) The process of the Bright Platinum Plating Company (of London), a modification of that of Roseleur, involving the introduction into the bath of certain substances, such as sodium chloride and borax, to ensure a bright deposit of the metal; and

(3) Boettger's method, founded on the electrolysis of a solution of the double chloride of ammonium and platinum in sodium citrate.

Each of these baths will yield satisfactory results for a time; but, as I shall endeavour to show, the peculiar difficulties met with in the practice of platinum-plating render it impossible to maintain the chemical integrity of these electrolytes, and, in consequence thereof, they soon become inefficient or inoperative by reason of contamination with the secondary products formed therein.

* Advance sheet. Read at the Meeting of the Chemical Section of the Franklin Institute, May 20, 1890.

I will endeavour in what follows to give the true explanation of the difficulties above referred to, and to indicate what, from a careful study of the subject, fortified by the results of numerous experiments, I conceive to be the only feasible method of overcoming them.

The first difficulty encountered is that of obtaining a bright, reguline, and adherent deposit of the metal, in which form only it will answer the demands of practice. There is no difficulty in effecting the separation of the metal from solutions of almost any of its compounds. Zinc, iron, and tin reduce it promptly by simple immersion, and this very facility of reduction is one of the reasons why, even by the method of electrolysis, the desired object is frequently accomplished only in an imperfect manner; for the electro-plater is obliged to meet and overcome its obstinate disposition to separate from many of its compounds in the condition of platinum black, lacking coherence and adherence, and therefore entirely unsuited for his purpose.

Another and no less serious difficulty arises from the insolubility of plates or sheets of this metal as anodes, when solutions containing platinum salts are submitted to electrolysis. In electro-plating with copper, silver, gold, and nickel, but little difficulty is encountered in practice on this account, since anodes of these metals are freely soluble in many solutions capable of depositing them when they are submitted to electrolysis, and the rate at which these anodes are respectively dissolved, approximates so nearly to that at which the metals are deposited upon the objects at the cathode, that the metallic strength of the electrolyte is maintained substantially uniform, and electro-plating solutions of these metals may be operated for a long time without requiring additions of metallic salts. The electro-deposition of the metals whose anodes are thus tractable is carried on industrially with success.

It results from this want of solubility of the anode that the metallic strength of the electrolyte employed is continuously being weakened, while the deposition of the metal is going on, and the conductivity of the bath is being continually modified thereby. The character of the deposited metal also is injuriously influenced by these constant alterations of condition in the bath; and, as the rate of deposition becomes slower and slower by reason of the gradual impoverishment of the metallic strength of the solution, it will be necessary to restore it by fresh additions of metallic salt. The practice in all the processes of electro-plating with platinum employed up to the present time, save that of Boettger, is to use for this purpose the tetra-chloride of platinum. With this single exception, all the solutions for the electro-deposition of platinum thus far made known, so far as I am aware, are made by treating the chloride with compounds of the alkalis, soda, potassa, or ammonia. Of these, the phosphates and oxalates of soda, or potassa, are in greatest favour, and a number of formulæ for preparing platinum-plating baths with their aid have been described. The resulting substance is commonly a double salt, such, for example, as the double phosphate of sodium and platinum; the double oxalate of potassium and platinum, &c., contaminated, however, in each case by the chloride of the alkali employed, which is formed from the decomposition of the platonic chloride. As often as it is found necessary to strengthen the bath, fresh additions are made of platonic chloride, which, by chemical interaction with the constituents of the bath, aided by the process of electrolysis, yields more alkaline chloride; and it follows that the bath, by reason of becoming surcharged with this foreign substance, and with other secondary products of electrolytic decomposition, ceases to yield bright, reguline platinum upon the articles to be plated therewith and must be discarded. It then becomes necessary to regain the platinum contained in the discarded bath, by one or another of several processes of reduction known to chemists. The platinum thus regained may be converted into chloride and utilised in the preparation of a

fresh bath, with which the same series of operations will be repeated. Boettger purposes to maintain his bath by fresh additions of his original solutions, but it must be apparent that the continued electrolysis of such a solution as he employs must be attended with the constant accumulation therein of alkaline chlorides from the same causes as those specified above. This rapid deterioration of the baths, therefore, involve their frequent renewal at the expense of time and labour, so that, in spite of the fact that there is a wide field for its application, it is principally for this reason that the art of electro-plating with platinum on the commercial scale has thus far been practised only to a very limited extent.

It occurred to me that it might be practicable to overcome the principal difficulty here set forth. Knowing the influence of extent of surface in promoting the solubility of substances, it appeared to me at least probable that if the platinum were exhibited at the anode in the form of platinum-black, or sponge, exposing thus an enormously greater number of points of attack to the electro-negative element or acid radical there set free, the result might be the solution of the platinum, and the problem of maintaining the metallic strength of the electrolyte would thus be solved. The correctness of this conjecture was verified by experiment. For this purpose a plate of porous battery carbon, previously treated with boiling hydrochloric and nitric acids, was saturated repeatedly with a solution of platonic chloride and dried. It was then introduced into a graphite crucible, finely divided carbon was packed about it, and the crucible and contents heated for about half an hour to bright redness. The carbon plate then contained within its pores platinum in a state of eminently fine division. Treatment with water, and with hydrochloric acid at boiling temperature, failed to leach out any platinum salt, showing that the previous treatment has sufficed to reduce all the platinum salt to the metallic state. The carbon plate was then suspended as the anode in moderately diluted hydrochloric acid, a platinum plate serving as the cathode. The acid bath was gently heated and a current of moderate strength was allowed to flow through it. There was a liberal evolution of hydrogen from the cathode, but little perceptible evolution from the anode. The acid solution gradually became coloured from the formation of platonic chloride, and after some time the bright surface of the cathode began to blacken and ultimately became covered with a thick coating of platinum black. It was thus demonstrated that an anode of platinum in a fine state of division is readily soluble in an electrolyte which yields chlorine at the anode when the same is electrolysed. This observation, so far as I am aware, is new. It proved, however, to have no practical value, since the solution of the anode demanded the presence of a large proportion of free acid in the plating-bath and the use of currents of such strength as to produce invariably the deposition on the surfaces to be plated, of black and non-adherent metal. Furthermore, it was found, as was to have been anticipated, that the physical condition of the anode exerted no influence whatever in the electrolysis of baths formed of the oxy-salts of platinum, from which the best results in electro-plating are obtained—since, in electrolysis such compounds, the acid radical separated upon the surface of the platinum black failed to exert any perceptible solvent action.

It was therefore necessary to devise some other plan for overcoming the difficulties herein described, and, after making a number of fruitless experiments, I was so fortunate as to find a plan which appears to offer a solution of the troublesome problem of electro-plating with the group of metals, whose anodes are insoluble, in a more satisfactory manner than any other that has hitherto been suggested.

The plan here referred to consists in employing platinum hydroxide for the purpose of maintaining the metallic strength of the plating-bath. For this purpose, the hydroxide, which is readily soluble in alkalis and in

many of the acids, may be introduced into the plating-bath from time to time and dissolved therein by stirring, or it may be permitted to remain in the bath in excess, the undissolved portion remaining at the bottom of the containing vessel, or it may be suspended in a canvas bag adjacent to or surrounding the anode of carbon, according as the nature of the electrolyte may indicate one or the other method to be the preferable one. As the solutions which yield the best results in plating are those of the oxygen salts, I have found it advantageous also to prepare these directly from the hydroxide. This method, I have found, is capable of yielding a number of electrolytic baths of platinum that will maintain their metallic strength approximately unimpaired during electrolysis, and without the objectionable features of introducing into them substances that will cause them to deteriorate by the accumulation therein of injurious secondary products of decomposition, as is the case where such baths are maintained by additions of platinic chloride or alkaline chloroplatinates, as has hitherto been the invariable practice. Referring now specifically to the properties that render the platinic hydrate useful for the purposes above indicated, the following points appear to be deserving of mention.

It is readily soluble in aqueous solutions of the alkaline hydrates, and in a number of acids, mineral and vegetable. In the treatment of the platinic hydrate with aqueous solutions of the alkaline hydrates, the former plays the part of a weak acid, forming compounds known as platinate, which are very soluble, and from which the platinum is not precipitated on the addition of an excess of alkali. A weak aqueous solution of sodic or potassic hydrate (but especially the last named) will dissolve a large quantity of platinic hydrate, at the ordinary temperature, though solution takes place more freely when heat is applied. These solutions have the advantageous features of being freely conductive of electricity, and of yielding bright, reguline, and adherent electro-deposits of platinum on metallic surfaces previously prepared to accept the same. Furthermore, with a current of moderate strength the platinic hydrate only is affected, as is shown by the pronounced evolution of oxygen at the anode, and by the total absence of gas at the cathode. Also, it is manifest from the free solubility of platinic hydrate in alkaline hydrate, even in the cold, that if free platinic hydrate be present in a bath of alkaline platinate, the alkali set free in the process of electrolysis will combine with this platinic hydrate to form fresh platinate. For this purpose it will be necessary either to have present in the bath at all times a small excess of platinic hydrate, which may remain upon the bottom of the containing vessel without interference with the plating, and which may be replenished from time to time, or to introduce at the end of the day's work a quantity of the platinic hydrate sufficient to restore the metallic strength of the bath to normal, assisting the solution of the metallic hydrate by stirring, and if necessary by the application of gentle heat. As I have found that the platinate solutions act best when they contain a considerable excess of free alkaline hydrate, being more conductive of the current and yielding the platinum more freely and in the best condition, the addition of the proper quantity of platinic hydrate at the close of the day's work in the case of a bath of considerable volume, or the addition of small quantities at intervals, in the case of a small bath, will be found to answer the desired purpose of maintaining the metallic strength of the bath approximately normal for an indefinite period. In a bath where considerable free alkali is present, the platinic hydrate added, as just indicated, dissolves very freely even in the cold. The important fact is to be noticed that the alkaline platinate solutions may be maintained and operated for a long time in the manner described, since no deleterious secondary products are formed by electrolysis to vitiate and render them inoperative, as will speedily be the case where the platinic chloride is used for this purpose. The

mineral acids (hydrochloric, nitric, sulphuric, and phosphoric acids) dissolved the hydroxide freely, as likewise do certain of the vegetable acids, notably oxalic acid, and form with corresponding salts of the alkalies double salts, many of which are soluble in water. Of the salts thus capable of being formed, however, so far as I have been able to determine by experiment, only a limited number appear to be adapted to yield a deposit of bright, reguline, and adherent platinum. The halogen compounds may obviously be prepared more conveniently by the direct solution of the metal in aqua-regia than by the method I have described, but as I have found the oxygen compounds of platinum to yield much more satisfactory results, I therefore exclude them from consideration.

Of the salts that may be formed from platinic hydrate by solution in acids (and in part by suitable combination with the corresponding alkaline compounds to form double salts) three only may be named as sufficiently useful to yield practically valuable results in plating. These are the phosphates, oxalates, and acetates, of which also it is practicable to form double salts with the alkalies, soda, potassa, and ammonia, which yield bright, reguline, and adherent platinum.

Oxalic acid, so far as I have been able to determine, of all the oxygen acids, is the best solvent of platinic hydrate, dissolving it even in the cold, but with great energy when aided by heat, and forming platinous oxalate, with evolution of carbonic anhydride. From this brownish black or deep blue solution (according to concentration) brilliant reddish brown scales of the salt separate abundantly and readily from the hot saturated solution. A saturated aqueous solution of the simple oxalate prepared from the hydrate, as above described, will yield bright, reguline, adherent platinum when electrolysed with a comparatively weak current, with evolution of carbonic anhydride at the anode. With a stronger current hydrogen also appears at the cathode. This bath may be maintained indefinitely at normal metallic strength by observing the precaution to add oxalic acid and platinic hydrate in small quantities from time to time; or by keeping constantly at the bottom of the bath some platinic hydrate, and adding oxalic acid in crystals or powder from time to time as may be required to keep the bath saturated; or, what is much to be preferred, making a supply of platinous oxalate from platinic hydrate in the manner previously described, and keeping an excess of this present in the bath at all times. This bath has the same advantages as are possessed by the above-described alkaline platinate baths, of being capable of indefinite maintenance at normal metallic strength, and of introducing no substances that will cause its deterioration by the formation of secondary decomposition products.

(To be continued).

NOTICES OF BOOKS.

The Law and Practice of Letters Patent for Inventions, with the Patents Acts and Rules Annotated and the International Convention; a Full Collection of Statutes, Forms, and Precedents, and an Outline of Foreign and Colonial Patent Laws, &c. By LEWIS EDMUNDS, D.Sc., F.C.S., F.G.S., Barrister-at-Law; assisted by A. WOOD RENTON, M.A., LL.B., Barrister-at-Law. London: Stevens and Sons, Limited.

IT has been the object of the author to produce a "comprehensive treatise upon the law and practice of patents for inventions," similar to that of Hindmarch, which, having been written as early as 1846, prior to the Acts of 1852 and 1883, is now to a great extent obsolete. In this attempt, as far as a non-legal reader can judge, he has been very successful.

With an admirable expenditure of research and labour he has collated all the principal judicial decisions bearing upon the subject, and from these materials, taken in conjunction with the existing statutes and rules, he has deduced a general survey of Patent Law. That this task has not been easy any reader may easily satisfy himself. The more gratitude is consequently due to the author, not merely from his own profession and from patent-agents, but from patentees, actual or prospective, and from patentees who may possibly be aggrieved by some existing patent.

The work is divided into three parts. The first deals generally with Patent Law and practice, with an account of the procedure for obtaining a patent—the application, specification, amendments, and oppositions, assignments, and licenses.

Part II. gives the Patents, Designs, and Trade Marks Acts of 1883—1888, so far as they bear upon patents.

Part III. gives an Appendix of Statutes, Forms, Foreign and Colonial Patent Laws—or, as we should prefer to put it, Colonial and Foreign.

On reading over this work with anything like the care which it fairly demands we cannot fail to be struck with the vast amount of litigation which our patent system involves. This is in part due to the circumstance that a patent is granted to every applicant, provided only he pays the fees and observes certain very simple regulations. Now, it is plain that no preliminary examination can prevent subsequent appeals to the Courts. In the United States and in Germany, where examination is very stringent, litigation on the validity of patents is by no means unknown. But we cannot help regretting the effrontery with which certain persons, especially aliens, will come forward and obtain patents for processes which have been in common use, and which have become public property. Thus, as recently as 1877, an agent patented as a "communication from abroad" the manufacture of aluminium sulphate by the action of sulphuric acid upon dried or powdered shales, and used the sulphate obtained in treating sewage!

In speaking of the publications of the Patent Office the author mentions with evident and most justifiable regret the discontinuance of the *Commissioner's Journal*, which not only gave information regarding every British patent, from the first application to its final expiry, but also the patent lists of foreign countries.

As a rule it has been the author's object simply to set forth the law as it now is, and not to suggest what it might, could, or would be. He writes, however:—"Patentees still suffer an anomalous and heavy taxation in the form of renewal fees, which begin to be payable before the end of the fourth year." Unless these are duly paid the patent lapses. To our certain knowledge this fact renders it much more difficult to dispose of a patent, since capitalists hold back in the hope that the patentee may fail to pay the fee. In the United States, on the contrary, when once the initial fee of 20 dollars has been paid the patent is safe for the full term of seventeen years.

The author mentions the complexity of the law prior to 1852, by which three separate patents were required for England, Scotland, and Ireland, and the heavy expenses thrown upon patentees, and adds that, "under the Patent Law Amendment Act the cost of obtaining a patent was greatly lessened, and there was a further reduction in 1883."

The expense of obtaining protection throughout the British Empire is, we believe, about £1400! We know of one invention which is lying dormant on this very account. What should have been done in 1852 was to devise an Imperial patent, obtainable either in London, Calcutta, Sydney, Cape Town, &c., or such other centres as might be agreed on.

It was very generally hoped when the Patent Act of 1883 was passed and the fees were made easier that a new vein of inventions would be tapped. This hope

does not seem to have been fully realised. The number of patents has indeed been largely increased, but a very large proportion are frivolous, whilst another proportion are held by aliens who formerly did not think it worth while patenting their ideas in Britain. We fear the British workman too generally seeks to rise in the world by strikes and agitations rather than by inventions.

It was originally held that the very meaning of the patent system was to introduce new arts and manufactures into the realm, but the law is now actually made the means of keeping them out. This is to a great extent effected by the "International Convention." Dr. Edmunds says that its "first principle was to ask only from each country the same treatment from subjects of each of the other countries as was accorded to their own subjects. The Convention was in no way based upon the principle of strict reciprocity." In fact it is based upon the principle of a completely "one-sided reciprocity," to the disadvantage of British subjects. Thus, suppose an Englishman wishes to obtain protection for an invention, say in the German Empire. His application will, in the preliminary examination, be "winnowed with so rough a wind," that to prove the novelty and utility of his ideas will be a hard task. We know an instance where the German Patent Office raised two objections to a desired patent. After prolonged negotiation it withdrew these objections as untenable, and immediately raised a fresh one of which no mention had been made in the first unfavourable report. Nor are the examiners of the American Patent Office any better to deal with. We remember a case in which they insisted that a terhydrate and a tersilicate were one and the same thing.

To return to Germany. Suppose the examiners report favourably, the patent is granted, subject, however, to the condition that the patent must be worked in Germany within three years.

In France there is no preliminary investigation, but the invention must be worked in France within two years, and the importation into France of articles patented in that country is forbidden under penalty of forfeiture.

The manner in which aliens are treated under the British law is in full contrast. Protection is granted without examination, and they are under no compulsion to work their inventions upon British ground at all. In fact numbers of them have evidently not the least intention of so doing, their object being simply to prevent anyone else from working such inventions in this country, though they go to work at once abroad. The remedy would be to enact that if any person, native or alien, holds a British patent for an invention and works it abroad, but does not work it in this country on a commercial scale within two years the patent shall become *ipso facto* void. The present state of things is a powerful argument in favour of Mr. Macfie and others, who are opposed to patent-right altogether.

We find it stated in a note that the Patent Commission, constituted under the Act of 1852, was to include, in addition to the Law officers of the Crown, certain other persons. "Application was in fact made to the Royal Society, the Chemical Society, and Institute (of Chemistry?) to advise on the selection of one member from each society to act as examiners." But as it appeared that these gentlemen were expected to give their services gratuitously the proposal fell through.

It is stated—and it has been repeatedly ruled by the Courts—that no patent can be granted for an invention which is in itself illegal or immoral. Yet we believe a patent was once granted for a machine to mould chicory into the shape of coffee berries. As the sole conceivable use for such a machine was fraudulent, this invention was surely immoral.

A vast amount of fraud, imposition, quackery, and sophistication would at once be rooted out if articles of food, drink, or substitutes for such articles, pharmaceutical products, and processes for their preparation, were deprived of protection by patent or trade-mark.

We regret that we cannot devote any further space to the consideration of this work and the questions which it raises. We must pronounce it indispensable to all who in any way come into contact with patents.

Bech Book for Test-tube Work in Chemistry, By H. T. LILLEY, M.A. London: Simpkin, Marshall, and Co. We have seen and heard "test-tube chemistry" spoken of with unsparing contempt, and here we find instructions for its performance! Who is in the right? It seems to us that a great number of preliminary examinations—especially if the substance in question is to be had in small quantities only—are best performed in test-tubes. If this is the case, instructions for the accurate performance of such operations are exceedingly useful.

The work is carefully written, the tests laid down are correct, and there are not a few remarks which will be of value to the student.

A Treatise on Practical Chemistry and Qualitative Analysis. Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., F.C.S. (London and Berlin), F.I.C., &c., Fifth Edition. London: J. and A. Churchill.

WHEN an elementary work on chemistry has undergone the ordeal of five successive editions it is evident that the task of the critic must be light indeed. We are bound at the same time to recognise that the book is admirably compiled, and that it presents a happy medium between the obscure conciseness of some text-books and the prolixity—often irrelevant—of others. Intelligibility and simplicity have been successfully aimed at. Directions for working and for the right use of apparatus are given more fully than is done in many manuals, and, what is of great importance, the whole has been carefully checked over by the author and his students. We must highly approve of the omission of speculative and descriptive matter, which, however interesting *per se*, is, in a treatise of this kind, "matter out of place."

The only drawback we can perceive is, perhaps, less the author's fault than his misfortune. The work is distinctly examinational, as will at once be seen from p. v. of the preface. We fear it must be admitted that the temporary awakening caused by the protest against examinationism set on foot by Mr. Auberon Herbert, though supported by thinkers who, perhaps, would agree on no other subject, has died away. It has been lost amidst the din of contending factions, and borne down by the mute unreasoning opposition of those interested in "passing," and in getting others to pass. Hence, if anyone takes an unexpected place in a competitive examination, the feat is greeted with jubilant cheering, as if the student had decomposed an element, discovered a new form of energy, or a biological generalisation wider than that of Darwin. So long as such a spirit prevails we shall never be released from those correlative enemies of research—the crammer and the examiner.

CORRESPONDENCE.

COMPLEX MINERAL ACIDS.

To the Editor of the Chemical News.

SIR,—In the "Notes on Valency, Basicity, Complex Acids, and Chemical Notation," which you were so good as to print from my MS. in the CHEMICAL NEWS (vol. lxi., p. 267), it should have been explained that the discussion of these subjects was there undertaken with reference to the question of mineralogical classification, as will be more fully set forth in a forthcoming treatise on

"Systematic Mineralogy." The conception of complex acids is not to be limited to oxygenised compounds, but, as will be seen, is also applicable to complex metalline species in which sulphur and selenium, arsenic, antimony, and bismuth are associated. The careful reader of these "Notes" will, moreover, perceive that where, in two places, the symbol Tl immediately precedes La, it is a mistake for Y (yttrium); and, moreover, that FeO₂ should be TeO₂ (tellurium dioxynid).—I am, &c.,

T. STERRY HUNT.

New York, June 30, 1890.

QUASSIA BITTER *versus* HOP BITTER.

To the Editor of the Chemical News.

SIR,—Mr. Adams, of Maidstone, some few weeks ago, in giving evidence before the Select Committee of the House of Commons appointed to enquire into the decline of the hop industry, described before that body a process which he stated would enable him to state whether foreign bitters had been used in place of hops in brewing, and a few days later read a paper before the Society of Public Analysts in which he stated that "boiling a 2½ per cent decoction of hops with 2½ per cent of sulphuric acid under a reflux condenser for two or three hours every trace of bitter is removed; but quassia and its allies are not at all affected by this treatment."

The statement that quassia and its allies are not at all affected by this treatment I repudiate strongly.

To substantiate my repudiation of Mr. Adams's process the following experiments were made:—

A 100 c.c. solution of quassia (B.P.) was taken and 50 c.c. of normal solution of sulphuric acid added, the flask was then attached to a reflux condenser, and boiled for three hours. Barium hydrate solution was then added to faint alkaline reaction, heated, and filtered. The filtrate was then freed from excess of barium hydrate by sulphuric acid, and filtered; the filtrate just exhibiting a faint acid reaction, which was then evaporated on a water-bath to about 200 c.c. Basic acetate of lead solution was next added until the point of saturation was reached, then boiled, and the precipitate filtered off, the excess of lead in the filtrate being very carefully precipitated by sulphuric acid. The slightly acid filtrate was then evaporated to its original bulk (100 c.c.), chalk added to neutralise any free acid, boiled, and then filtered. The solution thus obtained was compared with the original solution of quassia, with the result that the bitter was completely changed (to use Mr. Adams's expression) from that of a fixed bitter to that of a fugitive bitter.

Such being the case, I decided to boil some of the quassia solution for five hours, following the same treatment exactly, except that the last filtrate was evaporated to 50 c.c., and, when compared with the original, the bitter was found to be of a different character to that of the original; at least two-thirds of the original bitterness having disappeared.

Under these circumstances, the process is, in my opinion, worthless, and I have no doubt that if Mr. Adams will repeat the above experiment, and boil the solution of quassia with 2½ per cent of sulphuric acid for ten hours instead of five hours, at the end of that time he will most likely find that all traces of bitterness have vanished, even if taken up with chloroform.—I am, &c.,

WILLIAM JOHNSTON.

City Central Laboratory,
13, Fish Street Hill, E.C., July 14, 1890.

Parkes Museum.—In order to make the Parkes Museum, which is supported by the Sanitary Institute, available to all classes for the purpose of obtaining information on matters relating to hygiene and sanitary appliances, the Council have resolved to throw the Museum open free at all times except when meetings are being held.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cx., No. 26, June 30, 1890.

Partial Eclipse of the Sun of June 17.—J. Janssen.—The author communicates a letter from M. A. de la Baume Pluvinel, in which the latter remarks that so far he has not been able to detect any difference between the spectrum of the ring and the ordinary spectrum of the sun.

Photographic Spectrum of Sirius.—Dr. W. Huggins.—The author has for some time suspected the presence of a group of obscure rays in the most refrangible part of the spectrum of this star. In a photograph of Sirius taken on April 4 this group came out distinctly, and the author was able to make approximate measurements of the positions of six rays of this group. These obscure rays are as strong and broad as the rays of the ultra-violet series of hydrogen, and they probably belong to one and the same substance, at present unknown.

Researches on the Application of the Measurement of the Rotatory Power to the Determination of the Compounds Resulting from the Action of Malic Acid upon the Neutral Sodium and Potassium Tungstates.—D. Gernez.—Like the alkaline molybdates, the tungstates exert upon the rotatory power of malic acid a very well-marked action, the measurements of which show the compounds produced among simple numbers of equivalents of these bodies. The author's results are given in the form of a table.

The Action of Titanium Chloride upon Metals.—Lucien Lévy.—Titanium chloride being passed over silicon at white redness yields very hard cubic crystals of a steely whiteness. To obtain them it is necessary to operate in an atmosphere of pure dry hydrogen. Boron and various metals (excepting iron and antimony) may be substituted for silicon in this experiment. The crystals obtained are not readily attacked by reagents. Melting potassa alone dissolves them and produces an inflammable gas.

The Decomposition of Rocks and the Formation of Arable Soils.—A. Muntz.—The author has found the microbia of nitrification present on rocks, especially on parts which are in process of disintegration, and he ascribes to these organisms a considerable share in the formation of soils.

Identity in Composition of Certain Sedimentary Phosphates with Apatite.—Henri Lasne.—The author states that in the natural phosphates of sedimentary origin which he has examined fluorine is present in much larger proportions than it is commonly supposed. This is due to the defective analytical methods employed. The minerals in question contain 1 equiv. of fluorine to 3 of phosphorus.

Journal für Praktische Chemie.
New Series, Vol. xli., Part 7.

Certain Syntheses by means of Phenylcyanate.—R. Leuckart.—The author has examined the action of phenylcyanate upon aromatic hydrocarbons, upon the alkyl ethers of the phenols, upon the phenols, and upon the nitro-substituted aromatic amines and the amido-phenols.

Nitro- and Chloro-Derivatives of β -Methyl- δ -Oxyquinazoline.—H. Dehoff.—The author has examined the action of nitric acid and phosphorus pentachloride upon anhydro-acetyl-ortho-amido-benzamide. The results will shortly be made known.

MISCELLANEOUS.

Elizabeth Thompson Science Fund.—This fund, which has been established by Mrs. Elizabeth Thompson, of Stamford, Connecticut, "for the advancement and prosecution of scientific research in its broadest sense," now amounts to \$26,000. As accumulated income will be available December next, the trustees desire to receive applications for appropriations in aid of scientific work. This endowment is not for the benefit of any one department of science, but it is the intention of the trustees to give the preference to those investigations which cannot otherwise be provided for, which have for their object the advancement of human knowledge or the benefit of mankind in general, rather than to researches directed to the solution of questions of merely local importance. Applications for assistance from this fund, in order to receive consideration, must be accompanied by full information, especially in regard to the following points:—1. Precise amount required. (Applicants are reminded that one dollar (\$1.00 or £1) is approximately equivalent to four English shillings, four German marks, five French francs, or five Italian lire. 2. Exact nature of the investigation proposed. 3. Conditions under which the research is to be prosecuted. 4. Manner in which the appropriation asked for is to be expended. All applications should reach before December, 1890, the Secretary of the Board of Trustees, Dr. C. S. Minot, Harvard Medical School, Boston, Mass., U.S.A. It is intended to make new grants at the end of 1890. (The trustees are disinclined, for the present, to make any grant exceeding three hundred dollars; decided preference will be given to applications for smaller amounts.—(Signed) Henry P. Bowditch, President; William Minot, jun., Treasurer; Edward C. Pickering; Francis A. Walker; Charles-Sedgwick Minot, Secretary.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Tempering Brass.—Can any of your readers give me a recipe for effectually hardening or tempering small brass articles; the elasticity of the brass must not be disturbed, and whatever is used should not corrode the brass in any way? If the surface only of the wire is hardened this may be sufficient.—C.

Crown 8vo., price 6s. 6d.,

PRINCIPLES OF
GENERAL ORGANIC CHEMISTRY.

By Prof. E. HJELT,
of Helsingfors.

Translated from the German by J. BISHOP TINGLE,
Ph.D., Assistant in the Laboratory of the Heriot
Watt College, Edinburgh.

LONDON: LONGMANS, GREEN, AND CO.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that SIGISMUND PICK, of Szczakowa, Galicia, Austria, has applied for leave to amend the Specification of Letters Patent No. 5124 of 1887, granted to George Isaac James Wells, for "Improvements in the evaporating of liquors containing salts and in the separation of those salts."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 25th June, 1890.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed)

H. READER LACK,
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THE PHOSPHORESCENCE PRODUCED UPON THE FIRST CONTACT OF OZONE WITH CERTAIN FLUIDS.

By ERNST FAHRIG.

SOME years since, in experimenting with some new liquid preparations of ozone, I accidentally observed a phenomenon which immediately attracted my attention, and led me to make many more experiments upon the subject. But these further tests, instead of clearing up the matter by affording a definite explanation of the peculiar action produced, only mystified me the more; for they merely served to upset the various theories and explanations which have from time to time suggested themselves not only to me, but to scientific friends to whom I have mentioned the matter; and in my own view, they render no less untenable a theory which has been publicly advanced by some others who have independently discovered and worked in the same field, and to which I shall presently refer. Thus perplexed, I have resolved, with the Editor's kind permission, to publish an account of these experiments in this journal, in the hope that some among its wide circle of readers may be able to throw some fresh light upon the question.

My first observation of the phenomena was in the following manner:—I was in a dark room, and having in my hand a sealed bottle about three-quarters full of a preparation of ozone (in this instance a solution of ozone in water containing a small percentage of other substances, which I have found in the course of my experience are necessary to retain the ozone in solution), I, with no particular purpose in view, gave the bottle a vigorous shaking up; instantly I saw a soft phosphorescent glow of light floating above the surface of the liquid and permeating the space in the upper part of the bottle. Its appearance was only momentary; but on shaking the liquid up again immediately afterwards it was observed again, but in much diminished intensity. Further repetition failed to produce any results, but after an interval of ten days the liquid had apparently regenerated its power, and the same effects could be observed, though weaker. I observed the phenomena in another way, and obtained some especially remarkable results, by pouring a small quantity of an ozone solution into a glass beaker containing ordinary water. At first the cone-like projection of the solution where it falls into the water becomes luminous, and then the light suffuses the whole mass as the liquids become thoroughly mingled, and finally disappears. Similar experiments to this have since been successfully carried out by the gentlemen above mentioned as having worked in this direction; and it is doubtless upon consideration of this particular variation of the phenomena that they have based their theory.

Now, it does not seem possible that the luminosity can be due to a purely chemical action among the various inorganic constituents brought together, for a careful consideration of the properties and chemical reactions of these does not indicate the likelihood of any such action taking place. I have found, indeed, that it is essentially dependent upon some peculiar property of the ozone, and that it is in no wise influenced by the medium, solvent, or condition in which this is presented to the water. That is to say, the appearance of the phosphorescence is not thereby interfered with in entirety, although there is some difference of degree in the intensity produced. Thus, with preparations of ozonised oil the same effects occur, and also with ozonised air or the pure gas itself.

The latter is applied by means of a glass tube immersed in the water, and with this method there is a marked increase in the duration and intensity of the phosphorescence. Or an easy way, very similar to my first experiments, of observing the effect is to take a bottle partly full of ordinary water and confine ozone gas or ozonised air in the remaining space. When shaken up in the dark, the upper part of the bottle is seen to become permeated with the light.

Trying the experiment with other substances in place of ozone, I each time failed to produce the least appearance of the phenomena. Thus, chlorine, an element which in the striking similarity of its reactions to those of ozone exhibits a remarkable analogy to that gas—so much so, that it is extremely difficult to test or distinguish between the two—absolutely would not afford the slightest glimmer of light; although it, of all other substances, should be the most likely to produce analogous effects to those of ozone. To be quite certain upon this point, I applied the chlorine in a great many different ways and conditions, but always with the same negative results. Thus, free chlorine - gas, chlorine - water, chlorinated soda hypochlorides, chloride of lime, and ordinary bleaching liquors were all subjected to experiment, and in every case, as with numerous other substances, peroxide of hydrogen included, the already strongly established conclusion was confirmed, that the phenomenon is wholly and solely due to some remarkable action of the ozone, and to electrically produced ozone alone.

Having satisfied myself of this in a sufficiently exhaustive manner, I turned my attention to water into which the ozone preparations are introduced, and endeavoured to determine how variations in its quality and source might influence the effects. In this direction I met with a series of most strangely conflicting results. I found that some samples of water would duly give off the momentary glow of light, upon the application of the ozone, while others would not, but the most curious fact was that examination or analysis failed to discover any cause to which these and negative results might be assigned, or any explanation by which they might be reconciled. In river water the light was very good; in some from a deep well there was none whatever. In sea water there was none, and altogether there is a great and inexplicable uncertainty about the probable behaviour of any particular specimen of water, which makes it practically impossible to foretell the result when first trying the experiments with a new sample, although the characteristic impurities and conditions of the same may be well known and understood beforehand. It was owing to this same uncertainty that I was much vexed a short time since by failure in an attempt to exhibit the phenomena to a party of scientific gentlemen; while on the very next day I was able to succeed with almost identical materials and conditions. Hence, also, the great difficulty of arriving at any plausible explanation.

The theory before referred to, and which is apparently the most probable of any that has yet been suggested, is that the light is generated during the destruction or oxidation of the organic matter of the water, or in killing the bacteria or micro-organisms which it may contain. But I think this cannot be sustained in view of the tests made with different samples of water; for it is evident that were this the case, the appearance and intensity of the effects would depend upon the presence and proportional amount of organic matter in the water, which, however, does not seem to be at all agreeable with experience. In fact, I have found that water previously boiled and filtered, to free it from bacteria and other organic life, does not thereby become indifferent to the experiment, thus furnishing what would seem to be a very strong and direct negative to the aforesaid theory. But, in justice to its exponents, I should add that they deny it is possible to destroy bacteria by boiling, in which statement I understand they are supported by the great

bacteriologist, Dr. Koch, and they further affirm that this important office can only be effectually performed by means of ozone. If they are right in this contention their theory must be allowed to stand; but to prove it thoroughly it will be necessary to show a closer connection between the intensity of the phosphorescence and the observed proportions of micro-organic life than can at present be said to exist.

As to the light itself, I can only describe it as a soft phosphorescent glow, which quickly spreads through the mass of fluid or gas, as the case may be, and as quickly disappears. It is very similar in appearance to that of another phenomenon which I believe I was the first to observe some ten or twelve years ago, and of which also I have been unable to find any satisfactory explanation. It is that when the globe or bulb of an old incandescent lamp is lightly rubbed with the hand and then immersed in water, slightly warm, or simply breathed upon, a distinct light is observed to be diffused through the globe—in the dark, of course. I have laid especial emphasis upon the fact that the lamp must be an old one, because herein lies the peculiar interest of the experiment. For at first sight one naturally supposes that the same results can be obtained with an ordinary piece of glass; but this is not so; neither can any response to the experiment be excited in a new or unworked lamp. Of this I fully assured myself by making lamps specially for the purpose and subjecting them to tests to see if it was not some hitherto unobserved property of an exhausted bulb of glass. Therefore, as the vacuum, pure and simple, is not the cause, it would seem that the light is in some way dependent upon some sort of chemical change in the minute quantities of gases remaining in the bulb, produced by long contact with the incandescent filament. Gaseous compounds may be thus formed, which under the condition of extreme rarification, may have the property of phosphorescence when subjected to electric strain. Still this does not leave the reason for moistening the bulb at all clearly defined; though the function of this process is doubtless to accomplish a rapid discharge of the electricity generated by the friction of rubbing.

In conclusion, I may throw out a suggestion that the luminosity in the first case is due to a release of the energy stored up in the ozone at its creation, but I will say nothing as to its plausibility, or as to how it appears to meet the case.

ON THE ELECTRO-DEPOSITION OF PLATINUM.*

By W. H. WAHL.

(Concluded from p. 35).

PHOSPHORIC acid also is a solvent of platonic hydrate. A dilute aqueous solution of this acid will dissolve a small quantity of the metallic hydrate in the cold, and a much larger quantity when aided by heat. With increasing concentration the solvent power of this acid for platonic hydrate is correspondingly increased. The resulting solution of phosphate of platinum, according to the degree of concentration, will be wine-yellow to cherry-red in colour, and, with a comparatively weak current, will yield bright, reguline, and adherent platinum on metallic surfaces properly prepared to accept the same. The electrolysis of this compound also does not involve the formation of deleterious secondary products, the result of the operation being the separation of the metal at the cathode and of the acid radical at the anode—and of the elements of water which are evolved as gases respectively from anode and cathode. In the operation of the bath, therefore, it will become more and more acid

as the metal is withdrawn by the accumulation therein of the phosphoric acid set free at the anode. The maintenance of the metallic strength of the bath, therefore, may be effected as in the foregoing cases by having present therein at all times a small quantity of platonic hydrate, or by the addition at the end of each day's work of the quantity of the metallic hydrate which will be required to restore the amount of metal withdrawn. This bath must be worked very acid, and the solution of the platonic hydrate, to maintain the strength of the bath; must be facilitated by heating, as the solvent power of phosphoric acid for platonic hydrate is much inferior to that of oxalic acid. The double phosphates of platinum with certain of the alkalis may be formed, which will be capable of yielding a deposit of bright, reguline, and adherent metal, and of being maintained approximately at normal metallic strength in the same manner as I have set forth above. The best results I have obtained with the ammonio-platonic phosphate prepared by adding to the solution of platonic hydrate in phosphoric acid sufficient *aqua ammonia* to cause the same to give an alkaline reaction, which point will be indicated by the formation of a greyish precipitate that will not disappear on stirring; then restoring the acidity of the solution by adding free phosphoric acid in excess, upon which the precipitate readily dissolves. The resulting solution is yellowish or brownish, and yields superb plating; though, on account of the greater difficulty of maintaining its metallic strength by the solution of the hydroxide, it is not so well adapted as the oxalate for the work of electro-deposition on the large scale. The sodio-platonic phosphate, formed in a manner precisely analogous to the ammonia compound just described, will also yield bright, reguline, and adherent plating; but I have observed that the soda salt is less freely soluble than the corresponding ammonia compound, and consequently more difficult than the latter to maintain of normal metallic strength.

Platonic hydrate is only very sparingly soluble in strong acetic acid, and it is impracticable to facilitate the solution by boiling, since by persisting in this for a very short time the hydrate is decomposed and black platonic oxide is formed, which is quite insoluble in this menstruum. I have found, however, that an alkaline acetate bath may be prepared by the addition to the alkaline platimates above described of as much acetic acid as may be introduced without causing the formation of a permanent precipitate. But although the appearance and quality of the plating obtained with this bath leave nothing to be desired, the bath does not meet the requirements in respect of indefinite maintenance in normal metallic strength and uniform composition. This difficulty, however, as I have observed, becomes less and less pronounced as the bath is made more strongly alkaline, when it approximates more and more closely to the alkaline platimates; for it is obvious that in the presence of a large amount of free alkali this would unite with the acetic acid to form a simple acetate. The resulting solution would no longer contain sodio- (potassio-) platonic acetate, but sodic (potassic) acetate, sodic (potassic) platinate, and free alkali. Nevertheless the presence of acetic acid in such alkaline bath appears favourably to influence the quality of the plating yielded, giving the deposited metal a whiteness approaching that of silver; and since, furthermore, acetic acid yields only the elements of water and volatile compounds when electrolysed, and therefore does not contaminate the electrolytic bath by forming deleterious secondary products, I find its judicious addition to the above-described alkaline platinate baths to present some advantages.

The foregoing comprise the compounds that I have found to yield the most satisfactory results in platinum plating, and I will not tax your patience at this time by an enumeration of the results, either partially successful, or wholly unsuccessful, that I have obtained with a number of differently constituted compounds of this metal.

* Advance sheet. Read at the Meeting of the Chemical Section of the Franklin Institute, May 20, 1890.

I append directions for the preparation of the several electrolytic baths above described, and indicate what I have found to be the most favourable conditions for working them.

In conclusion, I desire to make known the fact, which was brought to my knowledge only within the past week, that my friend Prof. Wm. L. Dudley, of Vanderbilt University, Nashville, Tenn., has independently worked out the problem of electro-plating with iridium in a manner precisely analogous to that which I have herein described with platinum. Prof. Dudley has made no publication of his research, but, in a letter, informs me that he employed, as long ago as 1886, the following procedure, which I quote:—"A bath of the metal may be composed of either the chloride (IrCl_3), the double chloride of iridium and sodium, a double sulphate of iridium-ammonium. The latter was preferred. The bath was kept saturated with metal by suspending canvas bags in the solution (either near to or around the anodes) containing the hydroxide of iridium."

Directions for Preparing the Electro-Plating Baths.

For the alkaline platinate bath the following directions may suffice:—

Platinic hydrate	2 ozs.
Caustic potassa (or soda)	8 ozs.
Distilled water	1 gallon.

Dissolve one-half of the caustic potassa in a quart of distilled water; add to this the platinic hydrate in small quantity at a time, facilitating solution by stirring with a glass rod. When solution is effected, stir in the other half of alkali dissolved in a quart of water; then dilute with enough distilled water to form one gallon of solution. To hasten solution, the caustic alkali may be gently heated, but this is not necessary, as the platinic hydrate dissolves very freely. This solution should be worked with a current of about 2 volts, and will yield metal of an almost silvery whiteness upon polished surfaces of copper and brass, and quite freely. There should be slight, if any, perceptible evolution of hydrogen at the cathode, but a liberal evolution of oxygen at the anode. I have observed that the addition of a small proportion of acetic acid to this bath improves its operation where a heavy deposit is desired. The anode may be of platinum or carbon, and owing to the readiness with which the metal is deposited an excess of anode surface is to be avoided. Articles of steel, nickel, tin, zinc, or german-silver will be coated with black and more or less non-adherent platinum; but by giving objects of these metals a preliminary thin electro-deposit of copper in the hot cyanide bath, they may be electro-platinised in the alkaline platinate bath equally as well as copper. The bath may be worked hot or cold, but it is recommended to work it at a temperature not exceeding 100° F. It may be diluted to one-half the strength indicated in the formula, and still yield excellent results. The surface of the objects should be highly polished by buffing, or otherwise, prior to their introduction in the bath, if the resulting deposit is designed to be brilliant.

The deposition of platinum takes place promptly. In five minutes a sufficiently heavy coating will be obtained for most purposes. The deposited metal is so soft, however, that it requires to be buffed very lightly. A heavier deposit will appear grey in colour, but will accept the characteristic lustre of platinum beneath the burnisher.

The oxalate solution is prepared by dissolving 1 ounce of platinic hydrate in 4 ounces of oxalic acid and diluting the solution to the volume of one gallon with distilled water. The solution should be kept acidified by the occasional addition of some oxalic acid. The simplest plan of using this bath, and which requires no attention to proportions, is simply to work with a saturated solution of the oxalate, keeping an undissolved excess always present at the bottom of the vessel. An addition of a small quantity of oxalic acid now and again will be found

advantageous. The double salts of oxalic acid with platinum and the alkalies may be formed by saturating the binoxalate of the desired alkali with platinic hydrate and maintaining the bath in normal metallic strength by the presence of an undissolved residuum of platinous oxalate.

The double oxalates are not so soluble in water as the simple salt. The oxalate baths, both of single and double salts, may be worked cold or hot (though not to exceed 150° F.) with a current of comparatively low pressure. The metal will deposit bright, reguline, and adherent on copper and brass. Other metallic objects must receive a preliminary coppering as above. The deposited metal is dense, with a steely appearance, and can be obtained of any desired thickness.

The deposit obtained in the oxalate baths is sensibly harder than that from the alkaline platinate bath, and will bear buffing tolerably well.

The phosphate bath may be prepared by the following formula:—

Phosphoric acid, syrupy (sp. gr. 1.7) ..	8 ozs.
Platinic hydrate	1—1½ oz.
Distilled water	1 gallon.

The acid should be moderately diluted with distilled water and the solution of the hydrate effected at the boiling temperature. Water should be added cautiously from time to time to supply that lost by evaporation. When solution has taken place, the same should be diluted with sufficient water to make the volume one gallon. The solution may be worked cold or warm to 100° F., and with a current much stronger than that required for the platinites and oxalates. The ammonio- (and sodio-) platinic phosphates may be formed from the simple phosphate by carefully neutralising the solution of the phosphate with ammonia (or soda); then adding an excess of phosphoric acid, or enough to dissolve the precipitate formed, and an additional quantity to ensure a moderate amount of free phosphoric acid in the bath. The phosphate baths will be maintained of normal strength by additions of platinic hydrate, the solutions of which will have to be assisted by heating the bath, preferably at the close of each day's work. The metal yielded by the electrolysis of these phosphate solutions is brilliant and adherent. It has the same steely appearance as that exhibited by the oxalate solutions, but to a less pronounced degree. The physical properties of the deposited metal are in other respects like those described in connection with that obtained from the oxalate baths.

BLOWPIPE TEST FOR MERCURY.

By T. CHARLTON.

HAVING of late been engaged in testing a number of minerals for mercury qualitatively, I had occasion to employ the method recommended by Alexander Johnstone, F.G.S. (CHEM. NEWS, vol. lxxix., p. 221), and was highly pleased with the simplicity and delicacy of the method. In fact, I think that no blowpipe test has been devised equal to it for value for many years. There is, however, one small drawback to the method as given by Mr. Johnstone, and that consists in the likelihood of washing much of the sublimate formed on the cooler part of the tube down on the addition of the two drops of nitric acid and the one drop of potassic iodide, prior to obtaining the reaction. And it also happens at times that the effervescence caused by this addition of acid to the fusion mixture ($\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$) is so violent as to cause loss of the sublimate by washing it down the tube into the acid below.

To avoid these difficulties I have devised the following modified form of the test, which I can thoroughly recommend:—

First obtain the sublimate either by heat alone or by anhydrous fusion mixture, as recommended by Mr. Johnstone, and then, instead of adding nitric acid and solution of potassic iodide, simply drop into the tube a small grain of iodine (not an iodide). If this is quickly done the tube will still be warm enough to volatilise the iodine. If the tube has been allowed to cool before adding the iodine, then it will be necessary to apply a gentle heat, to cause the iodine to volatilise. As soon as the iodine comes into contact with the sublimate of mercury a bright scarlet mass is formed which is very characteristic of mercury.

Rocky Mountain Smelting Co.,
West Cliff, Colo., July 1, 1890.

ELECTROLYSIS OF DIFFERENT SUBSTANCES.

By P. L. ASLANOGLU.

1. *Water*.—On passing a current of electricity from six Fuller's mercury bichromate elements through ordinary London tap-water for about twelve hours, the hydrogen pole (platinum) became coated with a white residue, which, from time to time, fell to the bottom of the electrolysis tube. This white residue having been analysed, it was found to be calcium carbonate, which is contained in small quantities in ordinary drinking water.

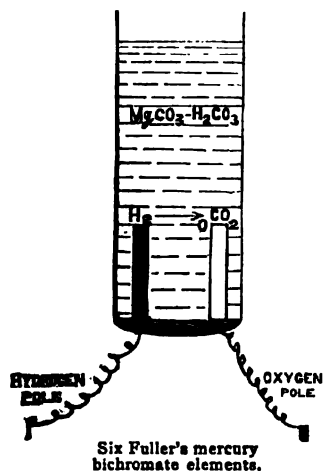
The oxygen pole (platinum) was free from any residue whatever.

During electrolysis hydrogen and oxygen were given off as usual.

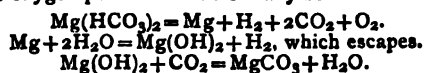
2. *Magnesium Carbonate* was suspended in distilled water and CO_2 was passed through the solution, and, after filtering, the clear solution was tested for magnesium, which it contained in considerable amount. The results obtained were the following:—

Hydrogen and oxygen given off as usual.

The hydrogen pole became coated with white residue, which fell to the bottom of the tube as in the previous experiment.



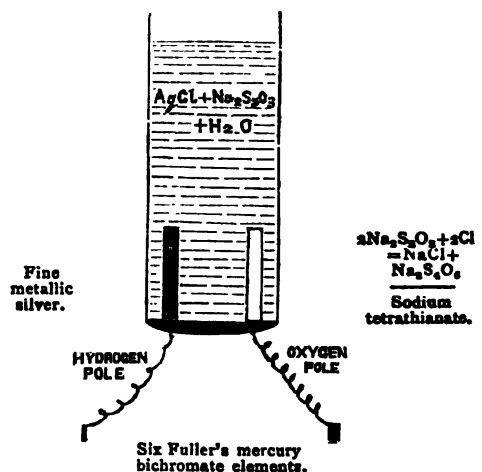
The oxygen pole was free from any solid matter.



3. *Silver Chloride* dissolved in sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), filtered, and electrolysed. The following results obtained:—

Only hydrogen given off, and a thick grey precipitate, turning at once to black, deposits on the hydrogen pole, which shakes off to the bottom of the tube. The smell

given off was that of sulphuretted hydrogen. The black precipitate was tested and found to be very fine metallic silver.



4. *Lead Sulphate* dissolved in a solution of tartaric acid, neutralised by ammonia (ammonia tartrate), and filtered. Hydrogen and oxygen were given off.

The hydrogen pole was coated with black residue, which smelt of ammonia, while the oxygen pole was coloured a golden yellow, and in the course of a few hours the solution was of the same colour, but gradually became darker.

5. *Barium Carbonate* and *Strontium Carbonate* were suspended in distilled water, and CO_2 was passed through the solution and filtered.

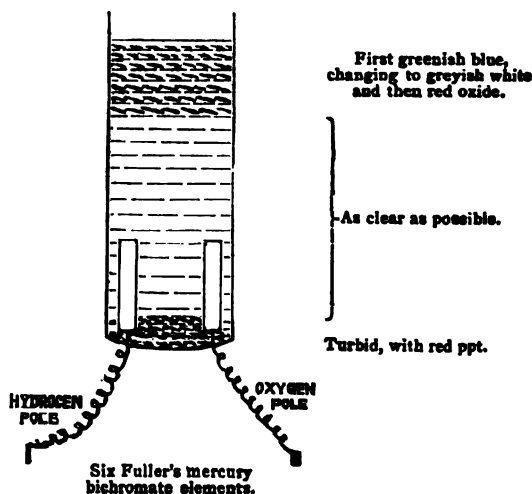
Hydrogen and oxygen were given off, whilst a fine white precipitate coated the hydrogen pole and fell off to the bottom of the tube.

6. *Zinc Carbonate* was suspended in distilled water, and, after passing CO_2 through it, was filtered.

Hydrogen and oxygen were given off with effervescence and bubbles of the two gases collected on the surface of the liquid.

The hydrogen pole was coated with a greyish black residue of zinc carbonate. The liquid became turbid, and a gelatinous precipitate floated on the surface, and by shaking the tube the precipitate fell to the bottom.

7. A mixture of *Ferrous Sulphate* and *Carbonate of Soda* was placed in a flask, which was then filled with



distilled warm water and CO_2 was passed through for half an hour. It was left to settle and the liquid was poured, leaving the precipitate at the bottom of the flask, and fresh hot distilled water was poured over it, and CO_2 was then passed for half an hour; this process was repeated six times, during which time CO_2 was passing through the flask so as to prevent the iron from oxidising. The last time it was left to settle for a few hours, and was then poured as quickly as possible through a filter, the clear liquid running into the electrolysis tube. The ferrous sulphate was thus converted into ferrous carbonate by carbonate of soda, and part of it was dissolved by passing CO_2 through. The liquid in the electrolysis tube was quite clear, free from signs of oxidation, &c. When it was subjected to a continuous current hydrogen and oxygen were given off. Both platinum poles were free from any residue from the beginning to the end of the experiment. The result is shown by the above diagram.

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UPON THE CARBOHYDRATES OF PEACH GUM.*

By W. E. STONE.

A CERTAIN class of vegetable products, known as "gums," or "mucous," or mucilage, yield, as the result of hydrolytic action, glucose-like bodies. These, whenever carefully studied, have, almost without exception, been identified as either *galactose* or *arabinose*. When heated with a dilute solution of sulphuric acid, gum arabic yields sometimes *galactose* and sometimes *arabinose*,† although it is not quite clear whether this is a specific characteristic of a distinct gum, or whether there may not be gums of different origins sold under the one name. The gum exuding from the bark of the cherry tree produces, by hydrolytic action, *arabinose*.‡ Tragacanth gum yields the same product.§ The mucilage occurring in the seed-coats of linseed, quince seeds, &c., yields also glucoses, which, however, have not been satisfactorily isolated or identified. A gum-like substance which can be extracted from lignified tissues, by alkalies yields, by hydrolysis, *xylose*.|| A gum exudes from the bark of the peach tree (*Persica vulgaris*) following injury, or from the fruit of the same when punctured by insects, which, with one exception, has not been studied. The wild peach tree, escaped from cultivation in the middle southern United States, produces this gum in considerable quantities, and from this source I obtained 200–300 grms., in air-dried weight, of gum as collected from the bark, and a somewhat less quantity from the fruit. The former was of a dark brown colour and contained many impurities, such as bits of bark, leaves, &c.; that from the fruit exuded in clear drops, which soon hardened on exposure to the air to transparent or semi-opaque tears, and was, of course, of a higher grade of purity than that from the bark.

This gum was soluble in water, by which it first became swollen to a marked degree, and in solution showed a slightly acid reaction, and a distinct, although not strong, *lævo*-rotation.

After my investigation had been in progress some time I learned of R. W. Bauer's results obtained from peach gum which was probably of European origin. By treating the same with a dilute solution of sulphuric acid he secured a crystalline sugar-like substance which possessed the specific rotation $(\alpha)_D = 76.02^\circ$, and which he regarded

as identical with *galactose*, although lack of material had evidently prevented confirmatory tests. From this he concluded that the peach gum contained the carbohydrate from which *galactose* is derived by hydrolysis. A preliminary examination of the gum in my possession indicated, however, that it also contained the substance from which *arabinose* is derived, as well as that mentioned by Bauer, and this was confirmed by further investigation.

The two portions of gum were examined separately, although all stages of the examination showed them to be of practically the same nature. As preliminary to a close study, portions of both gums were subjected to the furfural test for the presence of an *arabinose*-producing substance,* and to the mucic acid test for a similar source of *galactose*.†

By distillation at $125-130^\circ \text{C}$. with sulphuric acid kept at a constant density of 1.254, concentration of the distillate, and precipitation with dilute ammonia, the following data were obtained:—

Gum from Bark.—2.5 grms. yielded 0.1181 gm. of furfuramide, or 4.72 per cent.

Gum from Fruit.—2.5 grms. yielded 0.1214 gm. of furfuramide, or 4.84 per cent.

By oxidation with nitric acid of 1.15 specific gravity, mucic acid was produced as follows:—

Gum from Bark.—5 grms. yielded 0.618 gm. of mucic acid, or 12.36 per cent.

Gum from Fruit.—2.5 grms. yielded 0.423 gm. of mucic acid, or 16.92 per cent.

These results indicated the presence in the gum of those substances which yield *arabinose* and *galactose* upon hydrolysis, and the course of the investigation was directed towards isolating and identifying the same. 110 grms. of the gum from the bark of the peach tree were dissolved in 880 c.c. of dilute sulphuric acid of 1.03 specific gravity, and the solution heated on the water-bath for ten hours. At the end of this time, the liquid was of a dark amber colour, much humin-like substance had been separated, and the vapours gave an intense red colour upon paper moistened with aniline acetate, indicating the formation of furfural. The liquid was neutralised with barium carbonate, filtered, and evaporated, yielding a thick dark-coloured syrup which reduced Fehling's solution strongly. In the same way, 50 grms. of the gum from the peach fruit were dissolved in 400 c.c. of dilute sulphuric acid of 1.03 specific gravity, and heated during nine hours, with the same results as in the previous case.

The dark-coloured impure syrups thus obtained were boiled with strong alcohol for about an hour, whereby a dark gummy substance was precipitated. From this the clear alcoholic solution was decanted and again evaporated, after which crystallisation soon followed. In this way 21.3 grms. of a white crystalline product were obtained from the bark gum, or nearly 20 per cent of the material taken. From the fruit gum a proportionally smaller quantity was obtained. Both products were sweet, and reduced Fehling's solution strongly. After recrystallisation, the specific rotations of each were determined as follows:—

From Bark Gum.—3 grms. in a solution of 30 c.c. showed an average dextro-rotation of 19.16° , or $(\alpha)_D = 98.4^\circ$.

From Fruit Gum.—3 grms. in a solution of 30 c.c. showed an average dextro-rotation of 19.04° , or $(\alpha)_D = 95.2^\circ$.

These numbers indicated the identity of the two products, but did not correspond to the specific rotations of any of the known glucoses or sugar-like bodies, although that of the product from bark gum approximated the specific rotation of *arabinose*. They differed also decidedly from Bauer's result $(\alpha)_D = 76.02^\circ$. A mixture

* Contribution from the Laboratory of Purdue University.

† Claesson, *Ber. d. Chem. Gesell.*, xiv., 1270.

‡ Claesson, *Sachse*, u. Martin, *Phytochemische Untersuchung*, 69.

§ Sandenleben, *Ibid.*

|| Koch, *Pharmaceutische Zeitschrift für Russland*, xiv. Also Wheeler and Tollens, *Ber. d. Chem. Gesell.*, xxii., 1046.

* Stone and Tollens, *Ann. Chem. (Liebig)*, ccxlix., 227.

† Kent and Tollens, *Ibid.*, ccxxvii., 226

of two substances like arabinose and galactose, however, would give a polarising number like that obtained. Moreover, the preliminary tests for mucic acid and furfural had indicated the formation of both of these compounds. The next step therefore was an attempt to separate these products by means of fractional crystallisation into their constituents. By crystallisation from absolute alcohol each of the two original products was separated into several portions, the specific rotations of which showed a curious relation to that of the original substance.

From the sugar from bark gum, which showed the specific rotation of 98.4 , five fractions were obtained, which, in the order of their separation, showed the following polarising numbers:—

I. $(\alpha)_D = 97.5$	IV. $(\alpha)_D = 94.3$
II. „ $= 73.5$	V. „ $= 95.3$
III. „ $= 93.0$	

The sugar from fruit gum, which had the specific rotation 95.2 , was separated into two portions, which gave the following polarising numbers:—

I. $(\alpha)_D = 75.0$	II. $(\alpha)_D = 94.8$
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In both cases it is to be noted that a fraction was separated with a much lower specific rotation than the original without increasing the specific rotation of the other fractions. These fractions ultimately included all of the mother-liquor; hence it may not be assumed that a higher polarising sugar remained in solution. In the sugar from fruit-gum it is certainly remarkable that the original portion polarising 95.2° should have been resolved into one polarising 75.0° and another polarising at 94.8° , which latter number is practically the same as the original. There was no marked disproportion in the quantity of the fractions. The separations were made from alcohol at the ordinary laboratory temperature, which conditions could scarcely affect or change the specific rotations of the bodies in solution.

Of the fractions from the sugar from bark-gum, numbers I., II., and III., while not agreeing exactly with the polarisation constants for arabinose and galactose, still approached them. They were therefore re-crystallised and gave respectively the following numbers:—

I. $\alpha, (\alpha)_D = 98.8^\circ$
II. $\alpha, „ = 82.09^\circ$
III. $\alpha, „ = 98.9^\circ$

In like manner also the fractions from the sugar of the fruit gum were re-crystallised. I. was unfortunately lost by an accident, but its specific rotation, as already observed (75.0°), leaves little doubt that it would also have given a result similar to that of II. of the bark-gum product. II. showed after re-crystallisation the specific rotation 101.6° .

Nos. I. and III. of the product from the bark-gum were again re-crystallised and yielded a product with the specific rotation $(\alpha)_D = 102.3^\circ$. As results, therefore, of these repeated and tedious fractional separations, there were obtained, from the bark-gum, two products; one with the specific rotation 102.3° , which approximated very closely that of arabinose (104°), and a second with the specific rotation 82.09° , which is practically that of galactose. From the fruit-gum also we obtained two products which were undoubtedly identical with those from the bark-gum, and which, according to their specific rotations, were also respectively arabinose and galactose.

These comparatively pure products were now subjected to some confirmatory tests in order to leave no doubt as to their nature.

Arabinose being a pentaglucof, $C_5H_{10}O_5$, has, in common with xylose, the only other known member of the class, the characteristic reaction of producing furfural in large quantities when distilled with sulphuric acid.* Xylose, however, has the specific rotation $(\alpha)_D = 18^\circ - 19^\circ$,†

* *Loc. cit.*

† Wheeler and Tollens, *Ber. de Chem. Gesell.*, xxii., 1046.

and was therefore quite out of the question in connection with the body already described with the specific rotation 102.3° . 0.9246 grm. of the latter was distilled with sulphuric acid of 1.254 sp. gr. (the loss by distillation being replaced by a regular constant addition of water to the distilling flask), until the distillate no longer gave a distinct colouration on paper moistened with aniline acetate. The distillate being then concentrated by fractional distillation and treated with dilute ammonia gave a precipitate of furfuramide, which, on being dried, weighed 0.1843 grm., or 19.93 per cent of the weight of sugar taken. This result, taken with the specific rotation, leaves no doubt as to the identity of this product with arabinose. From a very small quantity a phenylhydrazine compound was prepared, which was, however, insufficient for re-crystallisation, and, in the impure state, showed the melting-point of 145° .

A well-known specific reaction for galactose is the formation of mucic acid when subjected to the action of nitric acid. The other portion of sugar from bark-gum, polarising at 82.09° , was heated on a water-bath with nitric acid of 1.15 sp. gr. 0.5025 grm. received 20 c.c. of nitric acid, and the whole was heated until two-thirds of the original volume was evaporated. 0.288 grm. of mucic acid was thus produced, or 57.3 per cent of the weight of sugar taken. A phenylhydrazine compound was also formed which melted at 154° . These reactions, coupled with the specific rotation, identifies the second product as galactose.

The gummy substance secreted from the tissues of the peach tree, as above described, contains, therefore, those bodies which, by hydrolysis, yield arabinose and galactose. The occurrence of these bodies together under these circumstances is the more noteworthy from the fact that arabinose and galactose represent two distinct classes of carbohydrates, the true glucoses and the pentaglucof, and are not usually found in such intimate connection with each other. The gum arabic is, I believe, the only other instance where such occurrence has been recognised, and in no previous case has the isolation and recognition of both these carbohydrates from a single homogeneous substance been accomplished.—*American Chemical Journal*, xii., No. 6.

ON A PHYSIOLOGICAL ACTION OF THE THALLIUM SALTS.

By Dr. J. BLAKE.

In a memoir presented to the Academy in 1887 (*Comptes Rendus*, cv., p. 1250) the author has demonstrated that on injecting the electro-positive elements into the circulation the number of the nerve centres upon which they react increases as does the atomicity of the elements.

In a communication recently made to the Academy by M. Rydberg it is demonstrated that the molecules of the electro-positive elements are the seat of one or of several systems of harmonic vibrations, which, in the mono-valent elements, are confined to a single system, but which, in the elements with stronger valencies, may be extended to two or even to more systems of harmonic vibrations in the same mol. This is a very important fact for biological reactions. The author has already published experiments demonstrating the great difference presented by the biological action of the salts of the same element when the valence of the mol. is increased, but as M. Rydberg's observations enable us to consider the question from a novel point of view, he recites the most important phenomena presented on injecting thallous or thallic salts into the blood.

Here we have two classes of salts of one and the same element. In the one class, the thallous salts, the mol. is found with a single system of molecular vibrations,

whilst in the thallic salts the mol. is the seat of several systems of harmonious vibrations. He merely reproduces here the most important facts presented by these experiments. He injected into the jugular vein of a rabbit 0.090 (grm. ?) of thallous sulphate. The result was an arrest of the passage of the blood through the lungs by the action of the thallous salt upon the pulmonary ganglia. After a few seconds the right side of the heart overcomes the obstruction, and the salt circulates through the entire body without giving rise to any symptom. The animal appears to be in a normal state. A second injection of the same quantity arrests the pulmonary circulation and the animal dies. The right side of the heart is found engorged with venous blood, and a few drops of arterial blood in the left cavities. By venous injection the salt only comes in contact with the most important nerve centres in a state of great dilution. To examine its action upon these centres it must be injected into the aorta. It was accordingly injected into the right carotid artery of a rabbit, the point of the syringe being directed towards the heart. There was injected 0.040 of thallous sulphate, then, at different intervals, 0.080, 0.200, 0.280, 0.350, without any apparent reaction on the nerve centres. There was then injected 0.770, and only then the salt came into contact with the pulmonary ganglia in a state sufficiently concentrated to arrest the passage of the blood through the lungs. Ten times as much of the salt was required to cause death by arterial injection as by venous injection. It seems that the reagent with a single system of vibrations did not meet in the most important nerve centres any system of vibrations which its own vibrations might either strengthen or enfeeble. It is only in the pulmonary ganglia that it finds vibrations with which those of the thallous salts are in relation, and the case is the same with all the mono-valent elements.

With the thallic salts the phenomena are very different. Here we make use of a salt the molecular weight and volume of which are much higher, and where the mol. is the seat of several systems of vibrations. We inject 0.007 of thallic nitrate into the jugular vein of a rabbit. After thirty seconds there was want of power in the limbs, the respiration slackened, and the animal is stupefied. After another injection of 0.007 the animal falls upon its side and struggles. Four minutes after the injection the respiration ceases. The right cavities of the heart were found engorged and the left empty (pulmonary obstruction); the ventricles still contract twenty-three minutes after the auricles are arrested (action upon the cardiac ganglia).

In this experiment the same action was observed upon the pulmonary ganglia as with the thallous salts, but when the salt had traversed the lungs and circulated in the whole body other nerve centres were found to be affected by the salt, even in its greatly diluted state (twelve times more diluted than the thallous salts), but these reactions upon the other nerve-centres show themselves more plainly in arterial injection. We inject 0.007 thallic nitrate into the aorta of a rabbit; after thirty seconds there was an increase of arterial tension from 100—180 m.m. (vasomotor centre); respiration slackened; after one minute, arterial tension from 170—190 m.m. with great oscillations; two minutes after injection respiration ceased without convulsions (direct action upon the respiratory centre). After death the contractions of the heart continue, and the arterial tension undergoes variation, as during life; three minutes after respiration has ceased the arterial tension increases from 40 m.m. to 100 m.m., and the same phenomenon was repeated three times before the heart stopped (action upon the vasomotor centre); the contractions of the heart continue for more than an hour after death; the ventricles and the auricles with a quite different rhythm (131 and 134) (action upon the cardiac ganglia) the lungs were hepatised (action upon the pulmonary ganglia). The contrast between the biological action of the two classes of salts of a single element could not be more striking. With the

thallous salts having only one system of molecular vibration there is only a single nerve system in which the action is shown; whilst with the thallic salts with mols. having several systems of vibrations there is not a single nerve-centre which does not experience their action, even when present in the blood in quantities less by 200 times than the thallous salts. The author believes that the spectroscopic will play as important a part in physiological research as it does in chemistry,—*Comptes Rendus*, cxi., p. 57.

CHEMISTRY AND MINERALOGY.*

By Professor E. H. RENNIE, M.A., D.Sc., University of Adelaide.

IN assuming the presidency of Section B of the Australasian Association for the Advancement of Science, it is my first duty to thank those who have done me the honour to elect me to the office, and to say that it will be my earnest desire to deserve the distinction by doing all in my power to forward the interest of the sciences which this section represents. While thoroughly appreciating the honour conferred upon me, I feel also a grave sense of responsibility—a responsibility to say something which may help to further the interests, not only of this section, but also of the Association, and, therefore, of Australasia.

The benefits to be derived from a meeting of this kind are doubtless, in a large measure, those which arise from conversation and social intercourse between men of like pursuits, and, in fact, we are often twitted with the preponderance of the social element. It will, however, be a great pity if those portions of the proceedings devoted to pleasure and relaxation are allowed to entirely eclipse the scientific objects of the gathering—if, in fact, by means of papers and discussions, we do not get some stimulus to more earnest work in the future.

In common with many others occupying somewhat similar positions, I have felt considerable difficulty in choosing a subject on which to address you. It has been customary in past years in the British Association for sectional presidents to give a general *resumé* of the more important researches and discoveries of the year immediately preceding; but, latterly, men in such positions have found themselves obliged by the ever-increasing rapidity of scientific discovery, and the consequent massing together of material, either to choose some educational theme, or to discourse on those aspects of the science to which they have themselves devoted special attention.

It will, I think, be granted that to the members of our Association any aspects or results of our science which have special reference to Australasia should be of peculiar interest, and I propose, therefore, to-day, in the course of a very brief address, first to inquire into some of the more important results which have been obtained by examination of Australasian products, and then shortly to touch upon some of those great chemical questions which are being more and more forced upon our notice by the far-reaching generalisations to which they point.

There are, of course, two lines on which an inquiry as regards Australasian products might proceed, viz., the purely utilitarian and the purely scientific. If, in this address, preference is given to the latter, it is not from any desire to undervalue the former, but partly because I have elsewhere given prominence to the importance of the application of science to practice, and because, as I believe, the greatest discoveries in chemical science in recent years, which have also been of great practical importance, have not been the result of accident, but the outcome of long and patient investigation in realms of work at one time most unpromising as regards useful issues, and, moreover, because one object of this Association, as

* Australasian Association for the Advancement of Science, Melbourne Meeting, 1890. Presidential Address in Section B.

I understand it, is the prosecution of scientific knowledge for its own sake, quite irrespective of the question whether it will immediately yield payable results or not. The perpetual cry, "*Cui bono?*" which would never be uttered by those who make use of it had any real idea of the history of the discoveries of the past, is most discouraging to those of us who are endeavouring to prosecute scientific work in these colonies, where it is exceedingly difficult to rouse interest in anything which does not immediately lead to material profit in one shape or another. May I not, in this connection, take the opportunity of urging upon all scientific teachers to use every endeavour to impress upon their students the historical developments of such discoveries as I have referred to?

Entering now upon the consideration of the chemistry of plant products, I am sure you will, in the first place, join with me in paying a hearty tribute of praise to the very valuable preliminary work which has been accomplished in the region of plant chemistry by our President and his collaborators, and to that more recent and most valuable bibliography of the subject contained in the "*Useful Native Plants of Australia*," lately compiled by Mr. Maiden, curator of the Technological Museum of New South Wales.

Among the more important products, those obtained from the "everlasting gum-tree" first claim our attention. In a remarkable series of researches carried out in the laboratory of the University of Bonn, Wallach has succeeded in reducing to something like order and system the confusion which has hitherto existed in our knowledge of that class of hydrocarbons known as the terpenes, and has revealed some most interesting facts about the relationships of these substances to one another, especially with reference to their optical properties. He has shown that some of these substances exist in what may be termed pairs, one of each pair dextro-rotatory, the other lævotatory, in its effect on polarised light. Thus he has found two pinenes, two phellandrenes, and two limonenes, the only difference between the two members of each pair being the effect on polarised light just referred to; but each set of two is characterised by the formation of derivatives distinct from those of any other two, and also from those of other hydrocarbons belonging to the terpene group. In the case of the two limonenes, however, there is a special and most peculiar characteristic. When simply mixed in equal proportions these two hydrocarbons unite directly to form another hydrocarbon, called dipentene, which is very different from either of the originals. This reminds one, of course, of the relationships between dextro- and lævo-tartaric and racemic acids. There is, however, this distinction, that dipentene differs much more widely from the limonenes than does racemic acid from the tartaric acids, and, moreover, there seems to be at present no known means of regenerating the original hydrocarbons from the product. My object in referring to these researches, however, is to point out that the oil of *Eucalyptus amygdalina* has supplied one of the missing links in the chain of discovery, Wallach having found that it contains lævo-rotatory phellandrene (this is at present the only source of this hydrocarbon), the dextro-rotatory variety occurring in the oil of *Phellandrium aquaticum*, and also in the oil of the bitter fennel in the south of France. The oil of *Eucalyptus globulus*, on the other hand, contains no phellandrene, but dextro-rotatory pinene, the two varieties of which are found in turpentines from different sources. The common constituent of both these oils is an oxygen-containing liquid called cineol, of formula $C_{10}H_{18}O$, and boiling-point about $176^{\circ}C$, which is the chief constituent of oil of wormseed, oil of cajuput, and is also found in oil of rosemary and other essential oils. This substance is identical with the so-called "Eucalyptol," about the presence or absence of which in oils produced by different firms there has, I understand, been a good deal of dispute. Wallach himself had at first some difficulty in isolating this substance from the oil of one of these (*Eucalyptus amygdalina*), ap-

parently owing to the presence of some disturbing impurity. The fact that it appears to be more easily isolated from the oil of one variety than from that of the other may probably have caused the dispute referred to; at any rate there can be no doubt whatever of its presence in considerable quantities in the oils from both the varieties of eucalyptus I have named, and probably it exists in the oils from other species also. It is a very interesting fact, however, that there should be a considerable difference between the constituents of the oils from these two trees, and there are indications of still wider differences between the oils from other species. The oil from *Eucalyptus Staigeriana*, for example, according to a report by Messrs. Schimmel and Co., of Dresden, contains an oxygenated substance (a ketone, $C_{10}H_{16}O$?) which imparts to it its pleasant lemon-like odour, and several other species of eucalyptus yield oils of a similar odour, probably due to the presence of similar substances. References to these will be found in Mr. Maiden's book, to which I have already referred. It is obvious that there is still abundant room for investigation in the direction indicated, an investigation too which has the additional merit of possibly leading to important practical results, some of the substances obtained having been highly spoken of as perfumes, while some, we know, possess considerable disinfecting power.

There are many other Australasian plants, besides the eucalyptus, the leaves of which yield essential oils, but scarcely any of these have received more than an imperfect examination, and here again is a wide field for work.

I may mention also here that some years ago I succeeded in getting a hydrocarbon, apparently a terpene of boiling-point $156^{\circ}C$, from New Zealand Kauri gum by passing steam over the roughly-powdered gum heated in a copper vessel. It would be interesting, perhaps, to re-examine this in the light of Wallach's researches, but up to the present time I have had no opportunity.

Leaving the essential oils, and passing to other classes of products, we find that *Eucalyptus viminalis* yields the well-known "manna." This has been lately shown by Tollens to contain over 50 per cent of raffinose, or melitose, one of the more recently investigated, and from a scientific point of view more interesting sugars, containing as it does at least eighteen atoms of carbon, and yielding a mixture of lévulose and galactose on treatment with dilute acids. I believe, though on this point I am not quite certain, that "manna" has also been found on other species of eucalyptus; if so, it would be well worth examining.

The alkaloids afford us a field almost untouched, so far as exact chemical investigation is concerned. So far as I know the only substances belonging to this class which have been at all carefully examined are those to be found in the bark of *Alstonia constricta* and the "*pituri*." Of the former several have been isolated and partially described by different observers, but especially by Hesse, who describes at least four; but all of them need further examination, especially as some, at any rate, possess very marked physiological activity. The alkaloid to which the peculiar effects of "*pituri*" are due has been isolated by Professor Liversidge, who describes it as a volatile liquid possessing characteristics closely allied to but distinct from those of nicotine, and having the formula C_8H_7N . This also needs further examination, but sufficient quantities of material are very difficult to obtain, and I understand Professor Liversidge has not had an opportunity to continue the investigation. There are numbers of plants which seem to contain principles of more or less poisonous nature, notably two natives of New Zealand, the *Coriaria ruscifolia* and *Corynocarpus levigata*. The former is said to be excessively poisonous to sheep feeding upon it, and extraordinary stories are told of the powerful physiological effects produced by eating the nuts of the latter unless they are first pounded and washed with water, a practice always observed by the natives. Mr. Skey, who examined these nuts, states that he suc-

ceeded in isolating a crystalline poisonous substance, which, however, appeared to him to be more closely related to the glucosides than to the alkaloids.

It is scarcely necessary to say that the complete isolation and thorough chemical investigation of physiologically active principles, whether of the nature of alkaloids or not, is of the greatest importance, if such principles are to be usefully applied to medicinal purposes. The scientific world owes a debt of gratitude to Dr. Bancroft, of Brisbane, for the valuable results he has obtained by physiological experiments with a variety of Australian plants, but the statement will bear repetition that from a chemical point of view a great deal still remains to be done.

As an instance of a glucoside, we have the active principle of *Smilax glycyphylla*, which is asserted by some to have considerable medicinal value, but which has not yet, so far as I am aware, been tried medicinally in the pure state, and in larger doses than can be conveniently administered in the state of infusion. It is a crystalline substance closely allied to phlorizin. By the action of dilute acids it yields phloretin and isodulcite, the latter, I need scarcely tell you, a substance of considerable interest and importance in connection with the question of the constitution of the sugars, and hitherto obtainable with difficulty from a few rare sources.

Colouring matters are not wanting as products of the Australasian flora, and many of these would, without doubt, yield results of great interest, if not always of great practical importance, were they subjected to close examination. You may be interested in examining these specimens of colouring matters from *Drosera whittakeri*, a South Australian species. These materials are capable of being used as dyes, and appear to bear much the same relationship to one of the methyl-naphthalenes as alizarin and its congeners do to anthracene.

My attention has been recently drawn to the fluorescent infusion yielded by the leaves of *Bursaria spinosa*; the fluorescence proves, on examination, to be due to the presence of considerable quantities of *asculin*, which, you will remember, is found in the horse-chestnut, and, as is stated, in the root of one other plant, the wild jasmine. This may prove to be an important source of this substance, should it ever prove to be of practical value.

Many of our gums and resins would doubtless repay close examination, and Mr. Maiden has done a great deal in collecting, classifying, and partially examining a large number of them, especially with reference to the quantities of tannin which they contain. One of the most closely examined of the resins is that obtained from the various species of *Xanthorrhoea*, which was at one time largely used as a source of picric acid. Its products of distillation, under different conditions, have not been thoroughly investigated, and might yield results of importance; and besides, the resin, originally examined by Stenhouse, appears to have been the product of one species only.

A great deal more might be said on this part of my subject, but I think I have said enough to show that there is still a wide field open if we can only find workers, but herein lies the difficulty. It has often occurred to me that outsiders may wonder why, in this land of great advantages, and with such an extensive field, there is not more original investigation. Why is there not an abundance of scientific papers, on all sorts of subjects, to be found in the proceedings of our scientific societies? It is true there are plenty of papers dealing with matters of Natural History, Geology, and kindred subjects, but very few involving long, accurate, and painstaking investigation in other branches of science. The reason is plain enough, viz., that those who have the will have either not the time or the means. Those of us who are most favourably situated as regards appliances have our hands full with the teaching, organising, and all sorts of outside work which is inevitable in colonies in a state of growth, and we have not, as yet, numbers of advanced students, such

as we find in older countries, who are only too glad to be entrusted with new lines of research. May we not hope that one effect of this Association will be to so interest young and old alike in the cause of scientific investigation, that such of the younger members as have time and means will come to our aid, and such of the older members as have sons, and can afford, will endeavour to give us a chance of showing what Australians can do in this direction by sending us their sons to be trained in some branch of scientific work.

Besides this difficulty of obtaining hands to work, there is often difficulty in obtaining material to work with; and here I have a suggestion to make, which may, perhaps, commend itself to you, and which, in case it is approved, will, I hope, be taken up by this section at a later stage in our proceedings. It is the custom in these colonies to apply to a paternal Government for assistance in almost everything, and this meeting owes its hearty thanks to the Government of Victoria for very valuable assistance rendered. Now, there are in most of the colonies, government organisations which specially deal with matters bordering upon purely scientific territory—geological, mineralogical, entomological, agricultural, and sanitary departments—not to mention others; and these departments have at their command men who could in many cases, at very slight expense, collect from time to time valuable material. Could it not be so managed that an individual, or individuals, thoroughly capable of dealing with some special investigation, and desirous of following it up, should apply to this Association, or to a specially appointed committee, for assistance; and might not such assistance take the form of accrediting such individual or individuals to the government of that colony from which he wishes to obtain material in such a way that the authorities would be induced to take steps for obtaining a supply of such material? In most cases the cost involved would be very small. The plan seems to me to be feasible, and it might, to some extent, prevent duplication of work, for it would become generally known that certain persons were carrying out such and such investigations. Of course, such applications would need to be governed by regulations; but should the suggestion meet with your approval, it will be easy to discuss the details at a later period.

(To be continued).

NOTICES OF BOOKS.

The Diseases of Crops and their Remedies. A Handbook of Economic Biology for Farmers and Students. By A. B. GRIFFITHS, Ph.D., F.R.S.E., F.C.S. London: G. Bell and Sons.

THIS work scarcely falls within the ordinary purview of the CHEMICAL NEWS; but we should neglect our duty did we not pronounce it a most serviceable publication. The majority of farmers, not to speak of the general public, have not the faintest conception of the extent to which we are robbed by tiny pests, of the very existence of which only specialists are often aware. The author tells us with perfect truth, that at least one-sixth part of the entire yield of farms is consumed by insects and fungi. Yet too many people, overlooking this definite demonstrable evil and its remedies, seek to remedy "bad times" by political or social agitation, and even sneer at the entomologist and the fungologist as triflers! Alas, in comparison, this name belongs with more propriety to the devotees of classical, historical, and ethical study.

A very remarkable fact is that the plants most useful to man, such as wheat, the potato, the turnip, the coffee tree, the vine, the sugar cane, &c., seem most open to the attacks of enemies, animal and vegetable, and to have the

least power of resistance. The vine, we read, "is liable to be attacked by some 350 parasitic fungi, in addition to the *phyllorera* and other animal pests."

The author's remarks on nomenclature are certainly not orthodox, though they are not without an element of truth. But the reason why the first describer's name is attached to a species—a practice condemned by no less an authority than Charles Darwin—is that sometimes a "reformer" takes a name already bestowed upon some plant or animal and gives it to another. Hence has arisen dire confusion.

Dr. Griffiths takes in succession the different crops produced in Britain, and describes under each the parasites by which it is attacked, and the remedies, so far as they have been ascertained. Here, however, there is room for a vast amount of research, much of which comes within the sphere of the chemist.

We must put on record our surprise at finding so scarce an insect as the swallow-tail butterfly (*Papilio machaon*) placed among destructive insects. It is far too rare to be of any importance in this respect. As regards the Death's Head moth, we must agree with Miss Ormerod, F.E.S., that its larvae seldom cause any serious amount of damage.

In his concluding remarks Dr. Griffiths emphasizes the importance of the microscope in the study of destructive fungi and insects, and especially recommends the instruments of Zeiss (of Jena). But many farmers and gardeners commit mistakes which a careful use of the naked eye might have prevented. We have known, *e.g.*, the useful lady-birds destroyed on suspicion of being identical with the potato-beetle.

Accidents with Mineral Oil Lamps. Report from Colonel MAJENDIE, C.B., H.M., Chief Inspector of Explosives to the Right Hon. the Secretary of State for the Home Department, covering a Joint Report from Sir F. ABEL, C.B., F.R.S., &c., and Mr. BOVERTON REDWOOD, F.R.S.E., F.C.S., &c.

These reports contain matter calculated to make the users of such lamps thoughtful. Minute particulars have been obtained concerning 29 lamp accidents. Here it appears that in 11 cases the lamp exploded spontaneously while burning normally. Hence the fault cannot always be traced to carelessness, to moving the lamp, attempting to replenish it whilst burning, or to extinguish it in some careless manner. Indeed, the death of Prof. Wroblewski—one of the most skilful and delicate experimentalists in Europe—shows that ignorance and awkwardness are not always to be blamed as the cause of the mischief.

Again we read that:—"In one-half of the cases in which it was possible to determine the flashing-point of the oil, this was about 10° and upwards above the legal standard." Sir F. Abel and Dr. Redwood even add that in some of these instances the explosion was of a more than ordinarily violent character.

It would be indeed deplorable if mineral oil lamps had to be abandoned or their use restricted on account of danger. Not only are they the cheapest known source of artificial light, but the steadiness of the flame recommends them to the student, and to the microscopist they are simply indispensable.

It is, therefore, fortunate that means are indicated in the Reports before us by which the dangers may be minimised. The reservoirs should be of metal, a suitable extinguishing apparatus should be provided so that persons present may not be tempted to blow down the chimney, and "all channels of communication between the burner and the oil-holder should be protected with wire gauze of 28 meshes to the inch." Lamps in which oil is supplied to the burner on the "bird-fountain" principle are considered free from danger if the tube through which the oil passes remains sealed by the

liquid. The wicks should be soft and not tightly plaited; they should be rendered quite dry before being put into the lamp, and should be only just long enough to reach the bottom of the oil reservoir. They should be so wide as to quite fill the wick-holder without squeezing. The reservoir should be quite filled before using the lamp; all charred wick and dirt should be removed before lighting, and the oil should be stored for use in vessels closely stoppered.

The subject is obviously of great importance, and we can only hope that the suggestions of Sir F. Abel and Dr. Boverton Redwood may be carried into practice by lamp-manufacturers and the public.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 1, July 7, 1890.

Oxidation of the Sulphur in Organic Bodies.—MM. Berthelot, André, and Matignon.—The authors, after criticising known methods, propose to burn the sulphuretted organic matter in oxygen at the pressure of 25 atmospheres in the calorimetric bomb, along with 10 c.c. of water. The combustion is instantaneous, and gives rise merely to dilute sulphuric acid whenever the organic compound is sufficiently rich in hydrogen. If it is not sufficient it is merely requisite to add to the body in question its own weight of camphor, or even a smaller dose. After the combustion the bomb is opened, the liquid which it contains is collected, and the interior is repeatedly washed out. The liquid contains in general nothing but sulphuric acid and some traces of nitric acid. It is precipitated with barium chloride and the barium sulphate is collected and weighed with the ordinary precautions. In some cases, in bodies sparingly hydrogenous, the combustion may be incomplete. This is indicated by the smell of sulphurous acid in the gases which escape when the cock of the bomb is loosened. The combustion in such cases is repeated, adding to the substance its own weight or half its weight of camphor. The author has obtained satisfactory results with such bodies as albumen, gluten, vegetable fibrin, and again with taurine and carbon disulphide. Free sulphur, however, even with the addition of naphthalene, evolved some sulphurous acid in its combustion.

Combustion-Heat of Certain Sulphur Compounds.—MM. Berthelot and Matignon.—The authors used the method mentioned in the foregoing paper in determining the combustion-heats of thiophene, taurine, and carbon disulphide.

Researches on Certain Saccharine Principles.—MM. Berthelot and Matignon.—Thermo-chemical determinations concerning erythrite, arabinose, xylose, raffinose, and the inosites.

New Researches on the Effluve.—P. Schützenberger.—The author describes his experiments on carbon monoxide. In a blank experiment a current of this gas, obtained by the decomposition of sodium formate by monohydrated sulphuric acid, freed from every trace of free oxygen, of carbon dioxide, and watery vapour, was allowed to pass in bubbles for six hours, and it was found that the weight of the tubes had not appreciably varied. In experiments when the gaseous current was kept at the same speed, but with the action of the coil, there was obtained a solid acid product which, when the gas was renewed only every three hours, gave carbon 42.1 per cent, hydrogen 1.4, and oxygen 56.5 per cent. On pro-

longing the duration of the action of the effluve upon one and the same portion of gas, the proportions of oxygen and hydrogen increase. The excess of these gases condensed is not in the proportions of water, the oxygen being in excess. On prolonging the action of the effluve upon one and the same portion of gas the proportion between the carbon dioxide formed and the total condensed product diminishes up to a certain limit. The elements of water do not penetrate the tube in their combined state, but separately, in consequence of a kind of electrolytic transference.

Action of the Various Alkaline Arseniates, in the Dry Way, upon Certain Metallic Sesquioxides.—C. Lefèvre.—The aluminium, chromium, and iron sesquioxides always yield an arseniate of the composition $2MO, KO, AsO_5$, as do those of the alkaline earths and of the magnesian series.

New Method of Preparing Basic Copper Nitrate and Crystalline Metallic Subnitrates.—G. Rousseau.—The author submits the two hydrates of neutral copper nitrate, along with an alkaline earthy carbonate, to the action of heat in sealed tubes. He rejects the formula proposed by Berzelius and Graham, and accepts that of Gerhardt, $3CuO, CuO, NO_5, HO$.

Double Phosphorus and Indium Bromides.—G. Geisenheimer.—The author has obtained $Ir_2Br_3, 3PBr_3$ in red crystalline needles. He has failed in producing a bromide corresponding to the double chloride, $Ir_2P_3Cl_{12}$. The double bromides differ from the corresponding chlorides in as far as the most stable of the former is $Ir_2P_3Br_9$, whilst the most stable of the chlorides is $Ir_2P_3Cl_{12}$.

On Certain Chromo-Iodates.—A. Berg.—M. Berg has obtained and described the magnesium, cobalt, nickel, and silver chromo-iodates, and subsequently that of copper.

On the Nitroprussiates.—M. Prud'homme.—The author gives three processes for obtaining nitroprussides. He recommends a mixture of sodium nitrite, 34.5 grms., and sodium hyposulphite, 15.5 grms., in 150 c.c. of water boiled with 41 grms. ferricyanide in 250 grms. water. If this liquid, when cold, is mixed with 108 grms. solution sodium bisulphite at 37° B. it becomes of a very deep red.

The Cause of the Alterations which Certain Compounds of the Aromatic Series undergo under the Action of Air and Light.—André Bidot.—The changes of colour in question are not due to any inherent properties of the compounds in question, but are occasioned by the intervention of foreign matters in infinitesimal proportions.

Transformation of Glucose into Sorbite.—J. Meunier.—The author hydrogenises glucose by the action of sodium amalgam, and obtains from 25 grms. 21 grms. of benzoic acetal, which corresponds to 35–40 per cent of sorbite.

The Hydrogenation of Sorbine and the Oxidation of Sorbite.—Camille Vincent and M. Delachanal.—The authors find that by hydrogenising sorbine they obtain sorbite. In attempting to produce sorbine by oxidising sorbite they have obtained glucose.

Synthesis by Means of Cyanacetic Ether.—A. Haller.—If the cyanacetic ethers are treated with sodium alcoholate they yield sodium derivatives, very susceptible of double decomposition. If these sodium compounds, dissolved or suspended in absolute alcohols, are treated with a current of cyanogen chloride, dicyanacetic ethers are produced.

Preparation of Certain Ethers by Means of Fermentation.—G. Jacquemin.—The author finds it possible to obtain ethers by sowing, e.g., the wort of malt with organised ferments.

Physiological Action of the Salts of Thallium.—J. Blake.—(See p. 44).

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 8.

The Preparation of the Crystalline Basic Copper Nitrate and its Identification with Gerhardtite.—L. Bourgeois.—On heating copper nitrate with urea in a sealed tube the author obtains very slender tablets of a pale greenish blue, which prove to be a basic copper nitrate. This substance occurs, along with malachite and cuprite, in specimens from Arizona, and has received the name Gerhardtite.

The Nitration of Propylbenzene.—R. Lespieau.—On causing a mixture of sulphuric and nitric acids to act upon propylbenzene the author has obtained a white crystalline body fusible at 238°. In the liquid separated from the crystals there appear oily products, which cannot be distilled, even in a vacuum. One of them is a yellowish liquid, having the odour of nitrobenzene.

Action of Ethyl Iodide upon Certain Acid Amides.—E. Duvillier.—The author examines the action of ethyl iodide in excess upon amidobutyric acid in presence of potassa. There is no production of betaine, but an abundant yield of diethylamidobutyric acid. If ethyl iodide in large excess (4 mols. and upwards) is allowed to act upon 1 mol. alanine dissolved in an alcoholic solution of potassa at 100° in a closed vessel there is not production of ethyl betaine, but of diethylamidopropionic acid.

Action of Trimethylamine upon Bromoisovaleric Acid.—E. Duvillier.—This reaction produces only a very small quantity of betaine, but an abundance of tetramethylammonium, and much dimethylacrylic acid. No iso-oxyvaleric acid is formed.

Combination of Ammonia with Metallic Permanganates.—T. Klobb.—According to the text-books, ammonia decomposes permanganic acid and its salts with liberation of nitrogen and separation of manganese dioxide or sesquioxide. This takes place on prolonged contact or at high temperatures, but it is possible to obtain crystalline compounds of certain permanganates with ammonia. The author has obtained such salts with copper, zinc, nickel, and cadmium. All these compounds dissolve without decomposition in dilute sulphuric acid, but their aqueous solutions, which are at first of a fine violet, soon deposit manganese oxide. The salts of zinc and copper are the most permanent. All of them detonate if struck with a hammer.

On Certain Products of the Distillation of Wood.—M. Vladesco.—In all the examples examined there were found, along with ordinary acetone, certain other higher acetones. It is probable that on operating upon larger quantities of material, propione or methylisopropylacetone might be recognised.

The Wines of Dried Grapes and their Total Proportion of Nitrogen.—P. Cazeneuve and L. Ducher.—The authors propose a determination of nitrogen, which is more abundant in raisin-wines than in wines made from fresh grapes.

On the Chloronitroanisols.—Louis Hugouneq.—An examination of dichloromononitroanisole, of the corresponding dinitro-compound, and of the trichloromono- and dinitroanisols.

Vol. iii., No. 10.

Vapour Density of the Selenium Chlorides.—C. Chabré.—It appears that the chloride $SeCl_4$ is dissociated into free chlorine and sub-chloride, and that Se_2Cl_2 , which is only decomposed partially if not in presence of an atmosphere of chlorine, is not decomposed at all if in contact with an atmosphere of this gas in the nascent state.

Sulphoconjugated Phenols Derived from Ordinary Camphor.—P. Cazeneuve.—Concentrated sulphuric acid yields in the cold, with monochloro-camphor, a total of sulphoconjugated compounds possessing the phenolic function. This formation proves that the terebenic series contains the benzene nucleus, and is a branch of the aromatic series.

Journal de Pharmacie et de Chimie.

Series 5, Vol. xxi., No. 3.

On a New Inosite.—MM. Maquenne and Tanret.—The authors have obtained racemo-inosite, which has the same relations to the dextro-rotatory and the levo-rotatory inosites as the paratartronic acid has to dextro- and levo-tartaric acids.

Presence of Magnesia in Acid Calcium Phosphate and Sodium Phosphate.—M. Schlagdenhauffen.—Acid calcium phosphate, if prepared in the ordinary manner from calcined bones, must of necessity contain magnesium phosphate to the extent of 1.02 per cent, and which is not fully eliminated. Solutions of sodium phosphate contain calcium and magnesium phosphates. In determining magnesia there should be used, instead of common sodium phosphate, a mixture of this phosphate, of magnesium chloride, and of ammonia, letting it stand for twenty-four hours, and using the clear liquid as precipitant.

On Quebrachite.—M. Tanret.—Quebrachite is not a hexatomic but a pentatomic alcohol.

Determination of Cantharidine in Insects.—J. B. Nagelvoort.—10 grms. of cantharides are moistened with a solution of soda at 10 per cent and let steep for six hours. The mixture is then acidulated with hydrochloric acid, placed in a Soxhlet apparatus, and exhausted with boiling chloroform (about 50 c.c.). When the chloroform is evaporated the remainder is washed with carbon disulphide, thrown upon a filter, and again exhausted with boiling chloroform. The solution is received in a small tared capsule, evaporated, and weighed.

Vol. xxi., No. 4.

Boric Acid in Articles of Food.—Contractors supplying preserved meats for the German navy have been officially forbidden to make use of substances containing boric acid. All persons who have experimentally consumed meat preserved with the aid of a powder composed of borax and soda have experienced derangements of digestion.

Sophistications in Russia.—According to *Le Caucase* the tea grown in Trans-Caucasia consists in large part of the leaves of a shrub named *Vaccinium arcto-staphylos* (?) which yield a decoction having some resemblance in taste to tea, but acrid and nauseating. These leaves are mixed up with inferior tea and with tea-leaves which have been already used. The *Nouvelles de St. Pétersbourg* adds that groceries, such as mustard, pepper, coffee, &c., often contain only from 1-20th to 1-10th of the substance which they professedly represent.

Vol. xxi., No. 5.

Assay of Commercial Tin Plate by Potassium Iodide.—Dr. Perron.—It is usually supposed that tin mixed with lead may be detected if we treat a spot of the surface with nitric acid, evaporate the white stannic stain produced, and then apply potassium iodide. In this operation there is a great risk of error if the nitric spot is either heated too little or too much in the process of drying. The author announces that he will indicate a novel reaction.

New Process for the Carbonisation of Wood in the Manufacture of Gunpowder.—H. Güttler.—The author injects hot carbon dioxide into the retorts during charring, and allows the product to cool in a cold atmosphere of the same gas.

Process for Rendering Thermometers more Sensitive.—C. Sache.—The author uses, instead of pure mercury, an amalgam containing 1 per cent of silver, which is a better conductor.

Vol. xxi., No. 6

Digestibility of Boiled Milk.—W. Raudnitz.—The use of milk boiled or even heated slightly above 100°

having been generally recommended in order to destroy morbid germs, the author has made comparative experiments with raw and boiled milk upon a young dog. He finds that the nutritive value of the raw milk is not appreciably less than that of boiled milk.

Action of Organic Acids upon Utensils of Nickel.—A. Rohder.—The author thinks that the use of such articles may be tolerated. Surfaces of 290 centimetres, after being exposed for twenty-four hours to the action of acetic acid at 2 per cent, only lost 24 to 29 milligrammes.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 52.

This number contains no chemical matter.

MISCELLANEOUS.

Institute of Chemistry.—The following are the names of the 43 candidates who passed the Institute Examination in Practical Chemistry held July 14 to 17 at Birmingham, Glasgow, Leeds, Liverpool, London, and Manchester:—J. Anderson, F. Boyce, H. Broadbent, F. Brownswort, A. Carey, G. C. Clayton, J. T. Conroy, A. W. Crossley, L. Crossley, H. E. Davies, E. V. Ellis, P. A. Estcourt, C. H. Field, A. W. Gilbody, W. Goodall, W. Greaves, A. Hall, G. Hefford, H. Ingle, S. Jackson, B. W. Jones, W. H. Joseland, Dr. J. W. Leather, J. H. Lester, J. G. Lord, H. S. Marsh, W. MacDonald, T. Newsome, S. Pickford, R. W. Prideaux, J. R. Paterson, W. Ramsay, G. H. Robertson, C. Smith, J. Spilsbury, J. H. Stansbie, J. A. Storey, J. J. Sudborough, M. Taylor, E. A. Wagstaffe, H. Watson, J. Wild, and J. H. Wilson.

Photographic Convention of the United Kingdom.—At this Convention there was presented a Report from the Committee on "Weights, Measures, and Formulae," drawn up by Mr. C. H. Bothamley. The Committee fully recognise the value of a decimal system, and also of a definite relation between the measures of weight and the measures of capacity. These features are possessed by the French or metric system, but also by a system of units in common use in England, the grain-weight and the grain-measure or fluid grain. It is merely necessary to reject the drachm, the scruple, and the minim, and express all weights in grains and decimal fractions of a grain, and all measures in fluid grains and their decimal multiples and sub-multiples. They remind their constituents that an exact equivalence between weights and measures exists only at one fixed temperature, and as concerns liquids of the same sp. gr. as water. Hence all solutions should be made up at 15° C. or else at 62° F. They recommend that formulæ should state the quantities of the ingredients to be contained in x parts of the finished solution and not the quantities to be added to x parts of the solvent. Hence they very properly advise photographers in making up a solution first to dissolve the ingredients in a quantity of the liquid smaller than the required volume of the finished mixture, making it up after cooling (if necessary) to the volume specified. These proposals, if acted upon, will prevent much confusion and error.

On Phenyl-Dithienyl.—Adolphe Renard.—Phenyl-dithienyl is formed along with phenyl-thiophene by the action of sulphur upon toluene at dull redness. It appears in colourless plates, fusible at 209°, and capable of subliming. It is very little soluble in alcohol, ether, petroleum essence, slightly soluble in chloroform and acetic acid, very soluble in boiling benzene and toluene. Its composition is $C_6H_5-(C_6H_4S-C_6H_4S)_2$. The author has examined its tribromo-, dinitro-, and disulphonic compounds.—*Comptes Rendus*, vol. cxi., No. 1.

THE CHEMICAL NEWS.

VOL. LXII. No. 1601.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

WHEN two oils are mixed together which separately yield insoluble products with sulphur chloride it is found that this reagent exerts a *selective* action, so that one of the oils is, relatively, more affected than the other, and I have no doubt a fractional separation may be made by adjusting the amount of chloride required for the quantity present of the more active oil. The quantity of soluble matter yielded by a magma to carbon disulphide, or removable by boiling in a solution of caustic soda, will depend on the amount of chloride used and also on the nature of the oils themselves.

Castor oil yields a small proportion of soluble matter and is so energetic in its action that we are obliged to dilute the chloride so as to moderate its effect. Rape oil or any similar oil, if used to dilute the castor oil, will only slightly modify its action; the effect of this oil is to deprive the rape oil of its allotted proportion of chloride and to become itself more firmly solidified; hence, when the magma is treated with CS_2 , the soluble portion will be proportionately richer in rape oil products as the quantity of castor oil is increased.

When the *yellow* chloride of sulphur acts upon an oil the chlorine is chiefly evolved as HCl , whilst the sulphur combines simultaneously with the dehydrogenised portion of the oil. I cannot speak definitely of what happens with those oils which do not yield insoluble products. The estimation of sulphur and chlorine retained in these purified insoluble products will assist us in many ways, so that I hope to supplement this part of the subject at an early date.

The total weight of the *dried* solid magma formed by sulphur chloride should always be noted, as it not unfrequently gives us an important insight into the nature of the substances we are dealing with; but a far more important clue is to be gained from the subsequent treatment with solvents—5 grms. lard gave 5.80 grms. solid magma, which was entirely soluble in CS_2 . This lard was prepared from the "flare" of the pig, under my own supervision. The iodine absorption was 52.6 per cent. I hope to obtain some purified lard oil from the same source at some future time, but the significant fact proved here is that lard oil should yield no insoluble product if pure.

The same quantities of lard and lard oil and chloride were used. Cocoa-nut oil is added to show the differences in weight yielded by fats giving no insoluble products and adulterated oils containing an oil which gives an insoluble product.

	SULPHUR CHLORIDE.		IODINE ABS., P.C.		REMARKS.
	Total weight, grms.		Original	Extract.	
	Magma.	Soluble.	oil.	from magma.	
Lard ..	5.80	5.80	52.6	47.40	Own rendg.
Lard oil ..	6.25	0.75	93.2	48.58	American.
" ..	6.19	0.48	89.9	52.06	English.
Cocoa-nut oil	5.14	5.14	—	14.70	

These results are very instructive. The iodine absorptions show that the oils or fats which yield no insoluble products are but little altered by chloride of sulphur, whereas a mixture of such an oil or fat will yield a soluble portion totally different in its iodine absorption and more closely approaching that of pure lard similarly treated.

Again, an oil or fat which is not solidified by chloride of sulphur gives an increase in weight very different from

oils yielding insoluble products, and the portion thus removed gives an iodine absorption quite unlike the original oils or mixtures. A mixture of cocoa-nut oil and cotton-seed oil may be put together having a low iodine absorption, but this treatment would at once reveal the nature of the mixture, as the cocoa-nut oil would be removed by CS_2 .

Lard oil, as used for lubricating, may be put together in two ways; animal fatty matter may either be added to cotton-seed oil, or the stearin from cotton oil may be in excess of what the oil naturally contains, and this may be added to animal fat, but by refrigeration and pressure we may recover the olein, when the iodine absorption of the substance left on the filter, as well as that of the olein, will help us to a solution of the problem. Animal fats or oil do not blend so intimately with vegetable fluid oils.

As regards lubrication, I do not suppose that there is much to complain of in this mixture, but when we pay £40 per ton for an article consisting mainly of an oil which can be bought for £20 per ton, the financial aspect is at least discouraging.

Bearing more directly on the chemistry of fatty bodies, and more particularly on the oleic and stearic glycerides, I may say that I am driven to the conclusion that chloride of sulphur shows us that we cannot regard these compounds in animal and vegetable oils and fats as having an identity of composition. Oleic and stearic acids from animal fats and concrete oils, when separated and purified, and subsequently converted into glycerides, behave as the original oils and fats, but if stearic or oleic acids be separated from cotton oil, or any similar oil, and subsequently converted into their corresponding glycerides, they behave with chloride of sulphur as before separation.

I was inclined to believe that this difference was due to the presence of some modifying constituent in certain oils or fats, or to a deficiency of glycerin; for the presence of this latter body is essential to the reaction. The probable expulsion of the glycerin will not account for the apparent anomaly in the behaviour of these acids.

This portion of the subject seems so important that I propose to re-examine the whole matter more minutely, so as to include the details in these papers.

The experimental case is briefly this:—A mixture of cotton-seed oil and lard was saponified, the fatty acids separated and re-converted into their corresponding glycerides, and purified by recovery from CS_2 solution. This mixture showed no difference when treated with chloride of sulphur, the cotton-seed oil and the lard had each recovered their own individuality as before.

The practical deduction is, that a mixture of oils may be so completely altered by time, exposure, or other accidental causes, that identity of its original composition seems hopeless. The mere loss of glycerin need introduce no embarrassment.

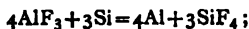
A BRIEF SUMMARY OF THE VARIOUS METHODS TRIED FOR THE PRODUCTION OF ALUMINIUM FROM 1886 TO 1890.

By H. N. WARREN, Research Analyst.

THE failures to procure several of the leading commercial articles at a less price, such as the caustic soda of the alkali manufacturers, the synthesis of alcohol for the distiller, the replacement of cane-sugar by saccharine, besides other compounds too numerous to mention, have of late led to the production of several eminent works, in which these experiments are clearly brought to the front, greatly aiding, no doubt, others working in the same direction. Still there are, in each of these works, gaps remaining to be filled, and it is therefore the author's intent to bring before those interested in the production

of aluminium at least a few of the more important experiments that have been undertaken both by himself and in conjunction with others, with the hope of obtaining further light upon this metal of the nineteenth century.

In the first instance I will confine myself as closely as possible to the mineral cryolite or its derivatives as the direct source or storehouse for the metal. One of the earliest experiments was the action of amorphous silicon upon that substance, which, although it yielded a negative result, being afterwards readily observed on account of the stability of that substance and its neutral reaction, nevertheless pointed to the direction of some allied substance presenting an acid reaction and less stable, and for it was substituted aluminium fluoride itself. Amorphous silicon thrown into melted fluoride of aluminium when at a high temperature reacts according to the following equation, yielding aluminium and silicon fluoride—



but aluminium being once formed and in contact with silicon fluoride at once decomposes it, yielding an alloy of silicon with aluminium containing about 70 per cent of the former substance.

The second lot of experiments comprise chiefly the injecting of the vapour of ammonia, ammonia oxalate, and the more volatile metals into the melted cryolite.

Experiments with the fluorides in contact with metallic copper, using as a reducing agent the hydrides of antimony, arsenic, sulphur, selenium, &c., have also been tried for the production of Al bronze.

For the production of ferro-aluminium metallic manganese in presence of iron has been made use of, also ferro-manganese, spiegeleisen, &c.

To manufacture the anhydrous chloride the incineration of a mixture of barium chloride and soda-alum has been made use of, and the introduction of magnesium for the replacement of the aluminium. The phosphides and sulphides have also been largely dealt with. With respect to arsenic the reaction afforded with this substance is more than striking. Absolutely pure aluminium was taken, melted at a red-heat, and metallic arsenic thrown on to its surface and impregnated with the same by stirring. A brittle arsenide of aluminium may be formed, but strange to say this compound is completely decomposed again on raising the temperature, even when out of contact with air, inasmuch that no arsenic hydride is produced when acted upon by dilute acids.

This reaction was at one time considered to be of value for the separation of aluminium from alloys containing the same. But quite a different phenomenon is observed in the case of alloys, an arsenical regulus being in every case readily formed. Aluminium in this respect may be compared to the action of metallic copper when in contact with sulphide of that element, and the marked difference observed when foreign impurities present themselves.

Bromides, iodides, and the subjecting of the oxide to all grades of temperatures when in contact with reducible gases have also been thoroughly experimented with. Various methods have been of late patented for the production of aluminium. Among a few of the most famous may be mentioned the action of common salt upon clay when in presence of zinc, and also that of heating to an enormous temperature a mixture of alumina, petroleum, and sulphuric acid, after which is introduced some fabulous metal which is stated reduces the aluminium; but the most curious part of these patents is the present price of aluminium when it can, according to the minds of several, be manufactured so readily. As regards the electroplating of aluminium the same difficulties present themselves. A cyanide of the metal would undoubtedly sound the most feasible, but to procure this compound is as difficult as the preparation of the metal itself. The cyanide, although stated by the various handbooks of chemistry to be unknown, is by no means so; for when a

rod of metallic aluminium is connected to the positive pole of a compact battery, a platinum plate furnishing the negative, and the extremities of each are brought into contact with a strong solution of hydrocyanic acid, aluminium cyanide is formed in the solution, which is entirely decomposed below the boiling temperature. Sulphocyanides, ferrocyanides, and all the compounds of aluminium, both organic and inorganic, have in short been thoroughly experimented with.

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ON THE COLOURING REAGENTS OF THE FUNDAMENTAL SUBSTANCES OF VEGETABLE MEMBRANE.

By M. L. MANGIN.

THE use of colouring matters in vegetable anatomy has not formed hitherto the subject of methodic investigations. Although the list of reagents used in microscopical studies grows daily, the absence of precise data on their composition, their chemical properties, and the conditions of their action renders the verifications of the results announced very much a matter of chance.

In the researches which the author has undertaken he has proposed to compare the action of the colouring matters with their composition, and to verify analytically the results obtained with colouring-reagents. He believes that by defining strictly the nature and the *modus operandi* of these reagents, it will be possible to arrive at a method for the qualitative micro-analysis of the tissues capable of superseding the empirical processes of colouration now used.

In this memoir he concerns himself merely with the fixation of the colouring reagents on the fundamental substances recognised in the so-called cellulosic membrane of plants, this fixation taking place without mordants in a neutral, alkaline, or acid medium.

The various colouring matters of the aromatic series may be divided into two categories: the one is formed of compounds in which a basic colouring-matter is united to various acids, mineral or organic; the other is formed of acid colours employed in the state of alkaline salts.

The substances of the first class fix themselves with a variable energy upon the pectic compounds, and thus manifest the acid function of the compounds. They colour neither callose nor cellulose. The author mentions the *azo-group*, e.g., Vesuvian brown and chrysoidine; the *diphenylmethane group*, e.g., auramine; the *triphenylmethane group*, such as Victoria blue, night-blue, magenta, Paris violet; then all the colours of the *oxazines group*, as naphthylene blue, Nile blue; of the *thiosins group*, methylene blue; of the *eurodins group*, neutral red; of the *saffranins group*, neutral blue, phenosafranine, magdala red, &c. The affinity of these colours for the pectic compounds is very unequal and feeble, as the presence of an excess of acid or glycerin is sufficient to decolourise the tissues more or less quickly.

The second class, formed of the alkaline salts, contains a number of substances which never colour the pectic compounds, but many of them fix upon cellulose and callose, proving the basic nature of these bodies. In this class we have an interest only in two groups, the *azo-group* and the *triphenylmethane group*.

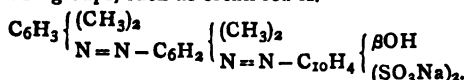
The *azo-group*, if we set on one side chrysoidine and Vesuvian brown, is chiefly formed of alkaline salts, among which we distinguish three important types.

The first type comprises the colouring-matters which only contain one *azo-group*, such as xyldine ponceau, the composition of which is—



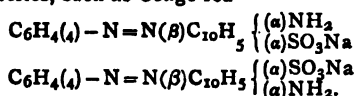
To this type belong aniline and toluidine ponceau, naphthorubine, &c., and the tropecolines. These substances colour the protoplasm yellow, but they have no action upon cellulose or callose.

The second type is formed of substances containing two azo-groups, such as orchil red A.



Here belong orselline BB., azorubine, naphthol black, the croceines, &c. The substances colour cellulose in a neutral or faintly acid bath, and have no action upon callose.

The third type contains colouring-matters of the benzidic series, such as Congo red—



To this type belong Bordeaux extra, Congo G R, Congo-corinth, delta-purpurine G, brilliant Congo G, resulting from the action of the sulphur compounds of naphthol upon benzidine; azo-blue, the Congo-corinth B, the benzo-purpurines, the rosazurines, where toluidine is substituted for benzidine, azo-violet, benzo-azurine, heliotrope, where dianisidine is substituted for benzidine, &c. These colouring matters, which are ordinarily precipitated by acids, dye cellulose and callose directly in a neutral or feebly alkaline bath.

The triphenylmethane group does not offer such definite relations between the colouring power and the chemical compositions. We distinguish here first a great number of bodies formed of hydrochlorates, sulphate, &c., which dye the peptic compound directly, and then a series of alkaline salts which we divide into three groups. The first group includes acid magenta, acid violet, Bayer's blue, Nicholson blue, &c., resulting from the respective action of sulphuric acid upon magenta, Paris violet C B, diphenylamine blue, or aniline blue. These substances do not colour cellulose, but some of them, as the soluble blues, and especially Bayer's blue, colour callose. The colourisation is the more active as the sulphurisation is more complete; thus 6 B blue, a mixture in which trisulphonated triphenylrosaniline predominates, is the most active of the soluble blues.

The second triphenylmethane group is formed of the alkaline salts of rosolic acid, which dye callose and cellulose directly.

The third group is formed of eosines, a salt of fluoresceine, such as eosine, erythrosine, phloxine, which colour nitrogenous matters strongly, but do not attach themselves to callose or cellulose.

The manipulative details will be described in a future communication.—*Comptes Rendus*, cxi., p. 120.

CHEMISTRY AND MINERALOGY.*

By Professor E. H. RENNIE, M.A., D.Sc., University of Adelaide.
(Concluded from p. 47).

If we inquire now what has been done in the region of mineral chemistry (I am speaking, remember, chiefly from a purely scientific point of view), we shall find, I think, that in this department even less has been accomplished. It is true we have a large number of analyses in official reports of one kind and another, but these have, for the most part, been undertaken and published purely from a commercial point of view, and there has been very little

careful and systematic analysis of the less common and less useful minerals, of which many varieties are to be found. So far as I have been able to ascertain there is scarcely any record of the discovery of the rarer elements. The only instance I have come across is the analysis of a sample of *monasite*, which was examined by Mr. Dixon, of the Technical College, N.S.W., and which he found to contain Cerium, Lanthanum, Thorium, and Didymium. In one or two instances some of the less rare elements have been discovered; for example, Mr. Mingaye, at the first meeting of this Association, proved the presence of considerable quantities of tellurium in some bismuth ores from Captain's Flat, N.S.W., and some years ago I showed that the appearance of brilliant yellow, reddish, and green colourations on white bricks made in the neighbourhood of Sydney were due to the presence of vanadium. I have found small quantities of vanadium widely distributed in many clays in the neighbourhood of Sydney. But is it not, to say the least of it, highly probable that in the large areas of mineral country which exist in so many parts of Australasia there are waiting to be found many minerals, possibly many new ones, containing either considerable quantities of rare but already known substances, or perhaps even new elements? That they have not been found I attribute to the fact that the search for minerals has been almost entirely directed to the finding of gold or other payable metals. We have heard a good deal of Broken Hill, perhaps there are some listening to me who are fortunate enough or unfortunate enough to know more about it than by mere hearsay, but it is scarcely to be doubted that a scientific search for and examination of minerals from the great silver field would yield results of great interest. Professor Masson and Mr. Kirkland have, I understand, examined a considerable number of zinc ores from that district for gallium, but so far without success. I have roughly examined the flue dust from the Dry Creek Smelting Works for germanium, but so far without finding any, but these negative results need not discourage us. You may be reminded in this connection that the Government assayer of N.S.W. reports the discovery of platinum, and probably therefore some of the associated metals, in some minerals from somewhere in the Broken Hill region.

This department of chemical science—I mean the search for new or imperfectly known elements—has acquired great interest and importance in view of the great impulse recently given to the study of the periodic law of Newlands and Mendeleëff by various chemists in Europe and the brilliant researches of Crookes on the nature of several of these so-called elements. It may not be out of place before bringing this address to a conclusion to review very briefly the more important results obtained in this direction during the past few years, the questions involved being of all absorbing interest to both chemists and physicists. It is evident that, whether justified by facts or not, there is a growing disbelief in the elementary character of the so-called elements, and this disbelief has arisen from results obtained in two different lines of research, namely, a more thorough study of the periodic law, and the spectroscopic investigations of Crookes and others.

One of the most important papers on the periodic law was that read before the British Association at Aberdeen, in 1886, by Carnelley. He brought out very clearly the analogies between the elements so called when arranged according to the periodic law and series of hydrocarbon radicles and their derivatives, and showed that it is possible to build up a series of compounds of two primary elements corresponding in many respects to the known series of elements, and he advances the speculation that all of the latter, except hydrogen, may be compounds of two substances, one with atomic weight 20, and the other with atomic weight -2, the latter being identical with the *ether* which exists all through space and matter as the medium of transmission of heat and light. Dr. Carnelley

* Australasian Association for the Advancement of Science, Melbourne Meeting, 1890. Presidential Address in Section B.

puts this forward merely as a speculation, and though the idea of a substance with negative atomic weight may be to others, as to myself, very difficult to grasp, there can be no doubt that his paper is a very valuable contribution to the study of the causes underlying the periodic law.

By the adoption of a form of zigzag curve Emerson Reynolds succeeded in indicating much more clearly than by the ordinary tabular system, the relations and contrasts between the various members of the different periods, bringing into prominence especially the following noteworthy points:—(1) The possibility that hydrogen is not the first member of Mendeléeff's first period, but the last—in other words, that there is still room for elements of lighter atomic weight than hydrogen. (2) The possible non-existence of Mendeléeff's ninth period, which includes at present only the metal *Erbium*; and (3) the inter-periodic character of the triplet group Fe. Ni. Co., Rh. Ru. Pd., and Ir. Os. Pt.

Crookes, in his lecture on the "Genesis of the Elements," adopted a slightly modified form of the curve proposed by Reynolds, and of it he says, "The more I ponder over the arrangement of this zigzag curve the more I become convinced that he who fully grasps its meaning holds the key to unlock some of the deepest mysteries of creation." Using it as an illustration, he sketches out a possible evolution of the substances known to us as elements from an original or primordial matter, which he calls *pyrolyte*, and in this sketch he explains the possible formation of such groups as the three triplets already referred to, and that of the Cerium metals, the characteristics of which he has done so much to elucidate. While on this subject of the graphic representation of the periodic law, attention should be drawn to a curious paper by the Rev. Dr. Haughton, read before the Royal Irish Academy in 1888, in which, by a geometrical representation of the law, he brings out some interesting and hitherto unnoticed points, and indicates in a very graphic manner the isolation of hydrogen and the points at which, in his opinion, there are still to be found missing elements.

The other line of investigation, which has led to serious doubt as to the accuracy of the hitherto generally accepted notions of the nature of the so-called elements, is the purely experimental, as developed by Crookes and others in researches on the rare-earth metals. By long and tedious experiments Crookes has succeeded in splitting up *yttrium*, for example, into several substances, which are, at any rate, spectroscopically distinct, but which are so closely related chemically that they are indistinguishable by ordinary methods. He believes it will be possible to obtain similar results with other substances, if only the right methods can be found; in fact, he has actually found indications of the commencement of a like separation in other cases than that of *yttrium*. Reasoning on these facts he has modified his views as to the character of the elements, and is now inclined to regard them, not as made up of a number of atoms of rigorously the same weight, but as consisting of groups of atoms of which the mean atomic weight is practically constant, but which differ in weight among themselves to a small but finite extent. This, in his view, would be the natural consequence of the generation of the elements from a primordial matter, and if I understand him aright, he believes that in such groups as that of the cerium metals, and others of which the members closely resemble one another, we have traces remaining of an imperfect differentiation into the distinct substances we have been accustomed to call elements.

In his Faraday lecture, delivered last year before the Chemical Society of London, Mendeléeff criticises somewhat severely these views as to the character and origin of the elements. He objects to the representation of the periodic law in the form of curves, as used by Reynolds, Crookes, and Haughton, on the ground that a curve as ordinarily used indicates a continuous and unbroken series of points, and that, therefore, at any and every point of such a curve, there should be a corresponding

element—in other words, this method of representation implies an infinite number of elements—so, at least, I understand his objection. It would appear, however, that this criticism is based upon a misconception of the real object of these so-called curves, which, I take it, are not intended to be understood in a purely mathematical sense, but simply as graphic representations of the periodic law, which enable us to see more clearly its prominent features. He points out further that the analogy between the series of elements and hydrocarbon radicles, worked out by Carnelley (thought previously indicated by Pelopidas) is weak in this respect, that whereas the series of natural elements involves an increase of mass as we pass from one member to another, the series of hydrocarbon radicles involves a decrease, and that therefore there is no true identity of periodicity in the two cases. This statement is, of course, involved in Carnelley's assumption of a negative atomic weight. As regards the existence of *helium*, an element supposed by Lockyer to exist in the sun, he points out that no attention is paid to the fact that the helium line is seen only in the spectrum of the solar protuberances, nor to the fact that the same line is wanting among the Fraunhofer lines of the solar spectrum, and therefore does not answer to the fundamental conception of spectrum analysis, and he further criticises other statements regarding the alleged spectroscopic indications of the decomposition of the elements. He does not, however, attempt to controvert Crookes's results, but says:—"From the foregoing as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed among mere utopias."

The supposition of Carnelley that the ether may be one of the forms of the primordial matter has been already alluded to. Recent physical investigations have thrown a wonderful light on the nature and functions of the ether, for a simple account of which I refer you to that fascinating book by Professor Lodge, entitled "Modern Views of Electricity." In his preface to the work he says "the evidence for (the existence of) ether is as strong and direct as the evidence for (the existence of) air," and he regards it as "a perfectly continuous, subtle, incompressible substance pervading all space, and penetrating between the molecules of all ordinary matter, which are embedded in it and connected with one another by its means." If there be such an all-permeating form of matter, does it not seem improbable that this substance should exist separate, distinct, and different from all other forms of matter, and having no share in their composition? Is it not more likely that it forms an essential part of all forms of matter known to us, and is it not possible that the known effects of heat, light, and electricity, for all of which this ether is undoubtedly the means of transmission, are either due to, or at least would be greatly aided by, its presence as a constituent part of the matter upon which the effects are produced? You are doubtless well aware that Sir W. Thompson has elaborated what is known as the vortex theory of matter, which represents the atoms as vortex rings formed of the substance of the ether, he having demonstrated that vortex motion is capable of conferring upon a fluid such as the ether the necessary rigidity. In speaking of this, Professor Lodge says:—"The atoms of matter are not so much foreign particles imbedded in the all-pervading ether, as portions of it differentiated off from the rest by reason of their vortex motion, thus becoming virtually solid particles, yet with no transition of substance: atoms indestructible and not able to be manufactured, not mere hard rigid specks, but each composed of whirling ether—elastic, capable of definite vibration, of free movement, of collision."

Whatever opinions we may hold on these subjects, there is not one of us but must feel, I think, that the scientific atmosphere is pregnant with coming discoveries, though the boldest prophet may well hesitate to predict

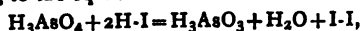
what they will be. In a few years chemistry, perhaps, will be reduced to a mere branch of the all-embracing science of physics, to be studied by differential equations and other mathematical processes yet to be invented. Already it is becoming more and more necessary for scientific chemists to be, not mere chemists, but also physicists and mathematicians. Let those of us who are not able to plunge into the more abstruse reasonings upon which some of the recently obtained results depend, content ourselves with doing our utmost to discover such new facts as lie within our reach, to aim at generalising these facts as far as possible, and so add to that storehouse of knowledge by means of which those possessed of greater powers of analytical investigation than ourselves may be able to elucidate the greater problems of nature: and let all of us who are members of this Association strive to make it such an influence in these colonies that Australasia may not be behind the rest of the world in its eagerness for scientific investigation and ambition to produce men who may rank among the great discoverers of future years.

A METHOD FOR THE REDUCTION OF ARSENIC ACID IN ANALYSIS.*

By F. A. GOOCH and P. E. BROWNING.

HOLTHOFF's development of Mohr's suggestion relative to the reduction of arsenic acid to the lower condition of oxidation by the action of sulphurous acid,† with the demonstration that arsenic acid can be evaporated even to dryness in presence of hydrochloric acid without danger of significant volatilisation, has placed the analysis of ordinary compounds of arsenic, both natural and artificial, within the scope of Mohr's classical and exact method of determination by titration with iodine. As Holthoff left the method, it is satisfactory so far as regards accuracy, and as modified by McCay,‡ who substitutes for the four hours' digestion heating for one hour in a pressure bottle, is eminently successful. In the account of the experiments about to be described we detail our experience in an attempt to shorten still further the process of reduction of arsenic acid by making use of hydriodic acid as the active agent instead of sulphurous acid.

In a recent paper§ we have described a method for the determination of iodine in haloid salts, based upon the action of arsenic acid, in the presence of sulphuric acid, according to the equation—



the iodine being completely volatilised, but leaving behind in the arsenious acid produced by the action the record of the amount of hydriodic acid originally present. This reaction we propose to utilise conversely, and to employ potassium iodide in excess, in presence of sulphuric acid, to bring about the reduction of the arsenic acid to arsenious acid, which may be determined, after neutralisation, by the iodine method. The conditions of the method are different than, in the former the hydriodic acid is entirely broken up by the action of the arsenic acid, and the iodine volatilises easily; while in the latter some hydriodic acid must remain in solution until a very low degree of concentration is reached, and remaining must exhibit its characteristic proneness to retain free iodine.

We find in practice that when a solution made up to contain sulphuric acid, an arseniate, and potassium iodide to an amount somewhat in excess of that theoretically demanded to effect the conversion of the arsenic acid to

arsenious acid, is boiled, iodine is evolved and the colour of the liquid passes from the dark red when the iodine is abundant through the various gradations of tint to a canary yellow, and then, as the sulphuric acid reaches a degree of concentration sufficient to determine by its own specific action the liberation of iodine, the colour again darkens, and if the process of concentration is continued, and much arsenic is present, crystals of arsenious iodide separate and form more abundantly on cooling. If evaporation is pushed still further the arsenious iodide begins to volatilise, and at the point where the sulphuric acid fumes the liquid loses all colour and the arsenic has vanished more or less completely. In one experiment conducted in this manner it was found, by the method to be described later, that of 0.3861 grm. of arsenic pentoxide originally present with 1 grm. of potassium iodide and 10 c.m.³ of sulphuric acid [1:1] the equivalent of 0.1524 grm. remained. In another similar experiment, in which, however, only a few m-grms. of arsenic oxide were involved, not a trace of arsenic remained at the end.

It is obvious that two points in this course of action demand examination at the outset. First, means must be found for removing the remnant of free iodine which is withheld by the hydriodic acid; or of rendering it harmless in the titration process to follow; and, secondly, the degree to which the solution may be concentrated without loss of arsenic must be fixed. In our work upon the converse of this process, we noted particularly the marked influence of the amount of sulphuric acid present upon the degree of concentration necessary to expel the iodine. We turned attention, therefore, at once to this point in the present case and investigated the effect of varying the proportion of sulphuric acid in solutions containing definite amounts of potassium iodide and potassium arseniate. The volume of the solution was made up to about 100 c.m.³ and concentrated by boiling until the colour was faintest. Then, to determine provisionally, and for preliminary purposes, the point at which volatilisation of arsenic was likely to occur, the concentration was continued until the arsenious iodide began to separate. The results are tabulated as follows:—

KI.	As ₂ O ₃ .	H ₂ SO ₄ [1:1].	Volume when colour was lightest.	Volume when AsI ₃ appeared.
Grm.	Grm.	C.m. ³ .	C.m. ³ .	C.m. ³ .
1	0.1900	20	80	33
1	0.1900	15	65	25
1	0.1900	10	40	19
1	0.1900	5	30	11

The amount of sulphuric acid which, considering rapidly in concentrating to the proper point, ease in neutralising the acid previous to titration, and general convenience in manipulation, seemed to be best was 10 c.m.³ of the mixture made by diluting the acid with an equal volume of water. This we fixed upon for use in future experiments, and set the limit of concentration at 40 c.m.³.

It is manifest from the phenomena described that when much hydriodic acid remains in the solution the last portions of free iodine cannot be completely removed by heat without volatilisation of the arsenic. We experimented, therefore, upon the effect of very dilute sulphurous acid upon the remnant of iodine in liquids constituted as described and concentrated to 40 c.m.³, the point of minimum colour, the solution of sulphurous acid which we employed corresponding approximately to centinormal iodine. We found that upon adding the sulphurous acid drop by drop to the hot concentrated solution the point at which the colour vanished could be determined without difficulty, but that if the solution was permitted to stand a single minute the colour of iodine returned, doubtless developed by the action of air upon the hot hydriodic acid. We adopted, therefore, the plan of at once diluting the solution with cold water as soon as the sulphurous acid had done its work and immediately neu-

* Contribution from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xi., July, 1890.

† *Zeit. f. Anal. Chem.*, vol. xxiii., p. 378.

‡ *American Chemical Journal*, vii., 373.

§ *American Journal of Science*, vol. xxxix., p. 188.

tralisating with potassium carbonate. When this mode of proceeding was followed we were unable to find evidence of reversion of arsenious acid to arsenic acid, magnesia mixture producing in the solution no precipitate of the ammonium magnesium arseniate.

Following out the same general lines, therefore, we proceeded to the quantitative examination of the process. Portions of a standard solution of the dihydrogen potassium arseniate were measured from a burette into counterpoised Erlenmeyer flasks of 250 c.m.³ capacity, and the increase in weight was taken as the measure of the actual amount of the solution employed. Potassium iodide in solution, and 10 c.m.³ of sulphuric acid [1:1] were added, and the liquid was diluted with water to a volume of about 100 c.m.³. A trap made as described in this paper upon the reverse of this process, by cutting down a two-bulbed drying tube, was hung in the neck of the flask to prevent mechanical loss, and the liquid was rapidly concentrated by boiling until the volume of 40 c.m.³, the point at which the colour of iodine had faded to a pale yellow, was reached. At this point the flask was removed from the flame, its sides and the trap were quickly washed down, the weak sulphurous acid was added drop by drop from a burette until the colour of the free iodine had just vanished, the liquid was immediately diluted with cold water, the free acid was nearly neutralised with potassium carbonate, and the point of neutralisation was reached and passed a little by the addition of the acid potassium carbonate. After cooling completely a definite amount of starch solution was added and the titration of the arsenious acid was proceeded with as usual, due correction being made for the amount of iodine necessary to produce the end colour into the volume of liquid and starch solution employed.

The value of the standard solution of the arseniate was fixed by two series of determinations. One series was made according to Levot's method of precipitating the ammonium magnesium arseniate and weighing as the pyroarsenate, modified, however, in that the precipitate was collected on asbestos in a perforated crucible and ignited after moistening with ammonium nitrate. In the second series McCay's modification* of Reich's method was followed, excepting that the silver arseniate was collected, dried, and weighed on asbestos in a perforated crucible. The mean of several closely agreeing determinations gave for the contents of 50 grms. of the solution in arsenic pentoxide as 0.3824 grm. by Levot's method and 0.3830 grm. by McCay's modification of Reich's process. We took the mean of these figures 0.3827 grm. as the standard of the solution.

The details of the experiments with this solution are recorded in the following table:—

KI taken. Grm.	H ₂ SO ₄ [1:1] taken. C.m. ³ .	As ₂ O ₃ taken. Grm.	As ₂ O ₃ found. Grm.	Error. Grm.
1.5	10	0.3861	0.3862	0.0001+
1.5	10	0.3862	0.3856	0.0006-
1.5	10	0.3861	0.3862	0.0001+
1.5	10	0.3860	0.3862	0.0002+
1.5	10	0.3863	0.3862	0.0001-
1.5	10	0.3862	0.3862	0.0000
1	10	0.1927	0.1922	0.0005-
1	10	0.1928	0.1922	0.0006-
1	10	0.1930	0.1925	0.0005-
1	10	0.1930	0.1927	0.0003-
1	10	0.1936	0.1929	0.0007-
1	10	0.1929	0.1928	0.0001-

Experiments in which smaller quantities of arsenic were handled were made similarly, excepting that the standard solution from which portions for the tests were measured was made by diluting the former standard ten times, and centinormal iodine was used in the titration.

KI taken. Grm.	H ₂ SO ₄ [1:1] taken. C.m. ³ .	As ₂ O ₃ taken. Grm.	As ₂ O ₃ found. Grm.	Error. Grm.
1	10	0.0383	0.0380	0.0003-
1	10	0.0383	0.0385	0.0002+
0.5	10	0.0383	0.0384	0.0001+
0.4	10	0.0383	0.0385	0.0002+
0.3	10	0.0383	0.0386	0.0003+
0.2	10	0.0383	0.0384	0.0001+
0.2	10	0.0076	0.0074	0.0002-
0.2	10	0.0076	0.0074	0.0002-
0.2	10	0.0038	0.0034	0.0004-
0.2	10	0.0038	0.0034	0.0004-

When the amount of hydriodic acid in solution is small, correspondingly small amounts of iodine are retained after concentration. In the following experiments colourless solutions were obtained, and, for the sake of comparison with the previous results, these solutions were neutralised and titrated without treatment with sulphurous acid, there being no apparent need for adding it in these cases.

KI taken. Grm.	H ₂ SO ₄ [1:1] taken. C.m. ³ .	As ₂ O ₃ taken. Grm.	As ₂ O ₃ found. Grm.	Error. Grm.
0.2	10	0.0038	0.0035	0.0003-
0.2	10	0.0038	0.0035	0.0003-

It appears, therefore, that the average error of the whole number of determinations (twenty-four) made by this process amounts to rather less than 0.0002 grm. —, falling between extremes of 0.0003 grm. + and 0.0007 grm. —. The entire amount of arsenic pentoxide handled in the twenty-four determinations was 3.7352 grms., and of this 3.7309 grms. were indicated in the titration as reduced to the arsenious condition. The loss 0.0047 grm. — the entire error of the process—amounts to 0.13 per cent of the amount taken.

Certain experiments were made to see whether the period of evaporation might not be dispensed with by so modifying the process that the entire amount of iodine set free in the action of the sulphuric acid, the arseniate, and the iodide might be re-converted at once by sulphurous acid to the condition of hydriodic acid. The conversion was apparently successful, but the results of the modification were several per cent below the truth, indicating that the digestion during evaporation, or the removal of the free iodine, or the combined effect of the two, is essential to the completion of the reduction of the arsenic.

The process as we recommend it may be summarised briefly as follows:—To the arseniate in solution are to be added potassium iodide in excess of the amount needed according to the equation to complete the reduction, and 10 c.m.³ of half and half sulphuric acid. The liquid is to be diluted to about 100 c.m.³ and boiled rapidly (with the precaution of trapping as described) until the volume is decreased to 40 c.m.³. The colour of free iodine is to be bleached by cautious additions of sulphurous acid (corresponding roughly to centinormal iodine) and instantly diluted with water and neutralised with potassium carbonate, the neutral carbonate at the first and afterward the acid carbonate. The whole is to be cooled and titrated as usual with iodine, using starch as an indicator. Its advantage is in the rapidity with which it may be executed, the whole operation being easily completed in a half-hour.

On Mannite Hexachlorhydrine.—Louis Mourgues.—The hexachlorhydrine of mannite, C₆H₃Cl₆, melts at 137.5°, boils at 180—185° under a pressure of 0.03 metre, and has the sp. gr. 2.060. It has a rotatory power at 20° of [α]_D = +18.32°. It is insoluble in water, very soluble in ether, benzene, chloroform, ligroine, &c., sparingly soluble in alcohol. Boiling concentrated alkalis do not attack it. It is dissolved by hot sulphuric acid, but reprecipitated on cooling.—*Comptes Rendus*, cxii., No.2.

* American Chemical Journal, vol. viii., p. 77.

THE DRY ASSAY OF TIN ORES.*

PART I.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

THE tin deposits of the Black Hills, discovered some ten years since, are beginning to attract very general attention, and the question how to treat the ores to the best advantage has become a pressing one. No systematic investigation of this subject has been made until quite recently, when it was taken up by the Dakota School of Mines, and the ores tested as to their tenour and proper mode of treatment. In the assay laboratory numerous determinations were made of the percentage of black tin in the ore bodies, and of the metallic tin contained in it. The occurrence of tin in the Black Hills being different from that in other parts of the world, the usual mode of procedure had to be somewhat modified.

The object of this paper is to give the results of the writer's effort to discover the best method of assaying the tin ores in the dry way. His task divided itself under three heads, in the following order:—

1. To test the different methods of assaying purified black tin in the dry way.
2. To study the influence upon the assay of the different minerals associated with the black tin.
3. To find by what simple and rapid means the cassiterite could most effectually be freed from its gangue.

The apparatus used was that to be found in any ordinary assay laboratory (the pulp-balance being sensitive to 1 m.grm.), as it was the aim to furnish quick and reliable methods with simple appliances. That dry assays of black tin have not the same degree of accuracy as wet assays is well known, but they suffice for the determinations necessary in metallurgical work. If great exactness is required, recourse must be had to one of the two wet methods,—that of Rose (fusing with sulphur and sodium carbonate, and converting the insoluble stannic oxide into soluble stannic sulphide), or that of Rivot (reducing the stannic oxide in a current of hydrogen to metallic tin, which is then readily soluble).

The cassiterite occurring in the Black Hills tin ores is quite pure, as is shown by the following analyses† of lode tin and stream tin:—

Lode tin:—

Occidental Mine	96.42	SnO ₂ .
Tin Mountain	97.50	"
First Find	94.70	"

Stream tin:—

Nigger Hill	92.60	"
Nigger Hill	93.00	"
Southern Hills	92.80	"

Stannite has lately been found in one locality. The cassiterite has an adamantine lustre, and its colour varies from brown to black, the light varieties being rare. The minerals associated with the cassiterite that are of interest to the assayer are iron pyrites, arseno-pyrites, in a very few instances galena and blende, quartz, feldspar, mica, tourmaline, garnet, and columbite (tantalite). The sulphides occur rarely, and then always in small quantities; quartz and silicates form the gangue; columbite (tantalite), although sometimes found in the same veins, can always be separated by hand-sorting. When it has accumulated in the stream tin deposits, which occasionally happens, it remains with the purified black tin. Bismuth, copper, and tungsten, which occur frequently in the deposits of other countries, are found very sparingly.

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 2.

† *Transactions of the American Institute of Mining Engineers*, xvii., pp. 595, 596.

I. The Assay in General.

Tin that is to be assayed in the dry way must be present in the form of oxide. The assay proper consists of applying in a crucible at a high temperature reducing and fluxing reagents, which bring the stannic oxide to the metallic state and convert the gangue into a liquid slag. The behaviour of stannic oxide and of metallic tin at an elevated temperature causes, however, certain difficulties, which make the results often less accurate than could be desired. These difficulties are:—

First. That some of the resulting metallic tin is liable to be volatilised.

Second. That metallic tin decomposes the alkali carbonates used as fluxes, forming stannates, which enter the slag.

Third. That at the temperature required to reduce the stannic oxide, other metallic oxides become also reduced to the metallic state and alloy with the resulting tin button, and vitiate the assay.

Fourth. That sulphates are reduced, or, if sulphides are present, they combine directly with the metallic tin and carry it into the slag.

Fifth. That the gangue in the ore is always siliceous. This causes loss, as the stannic oxide, while passing through the intermediate state of stannous oxide, combines with silica and silicates.

Sixth. That stannic oxide is liable, before its reduction has begun, to combine with the basic fluxes used in assaying and form stannates. This liability increases as the quantity of the flux is increased.

Thus it will be seen that the results can be too high (as when iron enters the tin button) or too low (as when tin is carried off in the slag as stannate, sulphide, or silicate), and that all impurities should be removed, if possible, before the actual dry assay takes place. The making up of the charge must also be regulated to counteract as much as possible the bad influences of the basic fluxes.

The crucibles used in assaying tin ores are the ordinary clay crucibles, the plumbago crucible, and the porcelain crucible. The naked clay crucible has the disadvantage that the basic fluxes attack the clay and form silicates, which are liable to slag some of the tin. From the results obtained by the writer it would seem that the material of the Battersea crucibles used by him must have been much better than that of the crucibles referred to by Berthier,* as no appreciable loss resulted from their use. P. Ricketts† recommends the lining of the crucible with chalk. This is probably to avoid the action of the basic fluxes on the acid material of the crucible, as the calcium oxide, being a strong base, protects the clay of the crucible from the corrosive action of the alkali, and thus hinders the formation of an alkali silicate. An outline of his method having been obtained from Dr. Ricketts, the lining was made from the so-called "prepared chalk" of the druggist in the following manner:—The prepared chalk was mixed with water in an enamelled iron dish to the consistency of cream. It was then allowed to stand, that the coarse gritty particles might settle and collect at the bottom. The chalk emulsion, now freed from impurities, was poured off and was ready for use. To line the crucible, it was half filled with the chalk mixture, the upper half being coated by giving the crucible a rotary motion, after which the excess of the liquid was poured off. The crucible was then placed bottom up for five minutes to drain, after which it stood for two hours to dry, and was then ready for use. The coating obtained was thin, uniform, and smooth. If the crucible be filled entirely with the mixture, and this be allowed to remain a little while before being poured off, the coating will be less uniform on the sides, part of the naked crucible will be exposed, and the lining at the bottom, being too thick,

* "Traité des Essais par la Voie Sèche," Liege, 1847, vol. ii., p. 485.

† "Notes on Assaying," 8th Ed., New York, 1886, pp. 88, 89.

will crack when it dries. If a greater thickness is wanted than can be obtained by one coat, it can only be properly put on, a layer at a time, as above, until the desired thickness is reached. The effect of the lining was disappointing; it did not, as will appear later, prove useful, but rather the reverse.

Another highly recommended lining is one of charcoal. The fluxes do not act chemically upon it, and its reducing power makes it unnecessary to add any charcoal to the assay; a reducing atmosphere is kept up during the entire operation. Berthier* states that he obtained 4 per cent more tin in a brasqued crucible than in a naked one, although even then he recovered 2 per cent less tin than was present.

The following method of brasquing, which differs somewhat from any of those described and recommended in the books, proved the most satisfactory. Pine charcoal is pulverised and screened through a 40-mesh sieve; the fine powder is then mixed with molasses and water in a suitable flat dish, and kneaded with the fingers until a homogeneous mass is obtained, which, when squeezed in the hand, coheres into a lump, and has not sufficient moisture to adhere to the hand.

Different proportions of molasses—the ordinary New Orleans molasses being used—and water were tried. Molasses alone with charcoal gave a sticky shiny mass, which cracked on the sides and the bottom of the crucible as it dried; two parts by volume of molasses and one of water behaved better, only the bottom cracking; three parts of molasses and one of water gave the desired mixture.

The crucible is moistened by dipping into water and quickly removing it. It is then partly filled with the charcoal paste, and this is pressed with the fingers against the sides and the bottom, a slight excess of material being used. Then a conical wooden plug, which has been dipped in water, is forced by hand into the charcoal paste and turned round and round, the excess escaping over the edge of the crucible. A few light taps with a mallet help to make the lining more compact. The wooden plug has a mark, and when this reaches the upper rim of the crucible the plug is withdrawn with the same rotary motion with which it was forced in. It has the form of a long cone, the point being slightly flattened. Its size is such that when forced into the crucible down to the mark, the lining at the bottom will be $\frac{1}{8}$ inch thick. This thickness decreases until near the upper edge of the crucible, where it is only $\frac{1}{16}$ inch. It is then rounded off until even with the inner edge of the crucible, and the sides are polished with a strong test-tube to prevent any particles of tin from adhering, and to obstruct the filtering of fluxes through it. In drying, it is best to place the crucible upside down; otherwise the lining is liable to separate from the wall, especially if it dries too rapidly. When a little skill has been acquired it takes four-and-a-half hours, including the preparation of the mixture, to line fifty Battersea crucibles, half of size F and half of size C.

It will be seen that this lining is quickly made; it dries quickly without cracking, and is hard when dry. After being in the fire, it is rapidly removed from the crucible, which can be used again, and is so compact and hard that it is difficult to break the thin upper edge with the fingers, while the thick lower part has to be broken with the hammer.

In summing up the subject of brasqued crucibles, it may be said that, although charcoal linings are perfect from a chemical point of view, their use has practical objections because of the separating of fine tin from fine slag in the pan. The results to be described will show that crucible linings are, in fact, unnecessary.

The plumbago crucible stands between the naked and the brasqued crucibles, for while the action of the fluxes on the clay is weakened by the plumbago, the neutral character of the latter is slightly modified by the clay

that binds it together. Plumbago crucibles are frequently used in the Cornish assay, but we shall see that this method is unreliable, and, as the plumbago crucible is expensive, more need not be said about it.

Finally, the porcelain crucible used by Levol has the same disadvantages as the naked clay crucible, although in a less marked degree.

II. Preparation of the Ore for the Experiments.

The more representative lode tin not being available in sufficient quantities to be made the basis of the following experiments, stream tin from the Nigger Hill district had to be resorted to. The cassiterite of the Bismarck district would have been the most desirable of all, as it is the purest. It is found in quartz, and has comparatively no deleterious minerals occurring with it. This makes the separation of the black tin from the gangue simple and perfect. The other lode tins, as well as all the stream tins of the Black Hills, have a number of minerals occurring with them which are difficult of removal; for instance, garnets.

The first pulverising of the ore was performed with the distance of $\frac{1}{4}$ inch between the faces of the sample-grinder. The crushed ore was then screened through a 40-mesh sieve. At the second grinding the faces of the machine were brought somewhat nearer together, and the sifting afterwards repeated. The operation was continued until the ore had all become fine enough to pass through the sieve, with the exception of some mica, which was thrown out. This gradual method was used in order to prevent the cassiterite from becoming too fine, as a large amount might thus have been lost in the washing of the ore. The pulp obtained was then roasted in a muffle to decompose any sulphides and arsenides that might be present. After roasting, and while still hot, it was thrown into cold water, to make silicates, not otherwise attacked by acids, decomposable. It was also hoped that the cassiterite might thus be made more readily reducible, an expectation which the event fulfilled. The ore was now boiled with nitro-hydrochloric acid, to remove all soluble metallic compounds; this was continued until no more iron was perceived to go into solution. The ore was then washed with hot water and transferred to the gold pan, where the panning was carried on irrespective of the loss of some fine tin which floated off with the tailings, giving them a chocolate-brown colour. As the main object was to obtain a pure black tin, the loss was unavoidable. The panning was continued until no more impurities were visible to the naked eye; under the microscope, however, particles of garnet with a little quartz were still visible. The black tin obtained was dried and intimately mixed by passing it repeatedly through a 20-mesh screen and rolling it on glazed paper. The now uniform ore was sampled down, and the final average sample pulverised in an agate mortar and put aside for chemical analysis. The weight of the purified black tin obtained, which was to form the basis of the experiments, was 7.968 grms. To find the size of the different particles, 500 grms. were taken and screened through different-sized sieves. The result of the mechanical analysis is given in Table I.

TABLE I.

Passed through sieve No.	Remained on sieve No.	Grms.	Per cent
40	60	90	18
60	80	80	16
80	100	65	13
100	—	265	53
—	—	500	100

The very brittle character of the cassiterite will be seen from this table, as 53 per cent of the entire ore passed through a sieve of 100 meshes to the linear inch, although as has been said, the greatest care was taken to grind in such a manner as to produce as small an amount of slimes as possible.

* "Traité des Essais," 1847, vol. II., p. 435.

III. Analysis of the Purified Black Tin.

In making the analysis of the average sample of the purified black tin, the Rose method was followed, as modified by Chauvenet, who substitutes potassium carbonate for the potassium carbonate commonly used. Two separate determinations were made, taking 0.5 grm. in each case with three grms. of a mixture consisting of equal parts of potassium carbonate and sulphur, and fusing in a No. 1 Royal Berlin porcelain crucible. The first sample was heated three quarters of an hour over a Berzelius alcohol lamp, and then for the same length of time over a gasolene lamp, after which the fused mass was treated with water in a beaker. Brown, gritty cassiterite now became visible at the bottom, showing that the decomposition was incomplete. The soluble potassium sulphostannate was then filtered off, and the filtrate acidulated with sulphuric acid and put aside; the residue on the filter was treated with hot dilute nitric acid, and the iron, manganese, and lime solution also kept. The residue was again fused with potassium carbonate and sulphur, but in a different way. The No. 1 porcelain crucible was placed within a No. 3 porcelain crucible, and this within a No. 6 plumbago crucible, the bottom of which had been filled with refractory material, that the porcelain crucible might be nearly as high as the plumbago crucible. The three crucibles were then each covered with a lid, and the fusion performed in a pot-furnace, heated with anthracite coal at a moderate red heat. This lasted one hour. The fused mass was then treated as before, and the resulting decomposition found to be perfect. The fusion for the second analysis was made directly in the three crucibles, and was complete in one operation. To make sure of this, the fusion was repeated, and, on acidulating the aqueous solution with sulphuric acid, the precipitate was found to have the milky white colour of sulphur.

The reason that the first fusion over the gasolene lamp was not successful, although prolonged until the fused mass became dry, must be sought in the fact that the air was imperfectly excluded. By fusing in a crucible which is enclosed in others, this exclusion can be entirely accomplished; in fact, upon removing the outer lid when the crucible had been taken from the fire, but had not yet cooled, a strong odour of sulphurous acid was perceived, showing that not only had the air been excluded, but that the fusion had taken place in an atmosphere of sulphur.*

The analyses were both made by the usual methods for separating iron, manganese, and lime, and the results corresponded so closely that they can be expressed by a common average:—

SnO ₂	86.24 = 67.84 Sn.
Fe ₂ O ₃	2.62
Mn ₂ O ₃	0.50
CaO	0.66
MgO	trace
Insoluble	9.39
99.41	

If this be compared with the analysis of the purest crystal of Nigger Hill Stream tin† that could be found,—

SnO ₂	93.06
Fe ₂ O ₃	3.08
Insoluble	3.90

100.04

it will be seen that the cleaning of the stream tin, as described above, was very successful, the ore sample showing only 2.4 times as much insoluble residue as the crystal.

(To be continued).

NOTICES OF BOOKS.

The Foundations of Chemistry (Grundlagen der Chemie).

By D. MENDELEEFF, Professor at the University of St. Petersburg. Translated from the Russian by L. JAWEIN and A. THILLOT. St. Petersburg: Carl Ricker.

FOR a work on the principles of chemistry to be worthy of the attention of any save the merest tyro is a rare event. No less rare is it for such a work to add anything to the reputation of its author, especially if he has already acquired a high and widely recognised standing. Yet such an exception is presented by the work before us. Not merely pupils but *savants* who have already "won their spurs" in the fields of research may read the work before us with pleasure and profit. Rarely has it been our good fortune to meet with an exposition at once so profound and so luminous, of the scope and methods of scientific research, of the ideas of matter, element, phenomenon, and reaction. We may here remark that the English language has lost by misuse a word which would have been very useful in discussing the philosophy of chemistry. Our "stuff" is the exact rendering of the German "stoff." Yet whilst "stoff" means "kind of matter," as distinguished from body or portion of matter, the English "stuff" has got to mean (a) a kind of textile fabric, (b) something of little value, and (c) rarely a kind of matter, simple or compound, as in "dye-stuff." We cannot avoid noticing with satisfaction that whilst 'οι πολλοι of scientific authors speak of all phenomena as being ultimately reducible to motion, Prof. Mendeleeff writes that we endeavour to conceive of phenomena as motion—an important distinction.

The author does not entertain the view that our present elements have been developed from any simpler state of matter or that they are capable of mutual transition. He writes:—It has been established by spectral analysis that the simple bodies exist in the most remote stars, and that they bear the highest temperatures which can be reached without decomposition.

The facts elicited by the spectroscopic examination of the stars seem to us to admit of a different interpretation. In proportion as the stars are more brilliant and in appearance hotter, the smaller is the number of elements recognised in their spectra, whilst those which are less luminous and presumably cooler display richer and more complicated spectra. Hence it seems not unreasonable to conclude that the latter class contain other and more numerous elements than the former—elements which can exist only at lower temperatures.

Prof. Mendeleeff considers that the next great task of science is to constitute molecular or chemical mechanics. The general laws of mechanics recognised by Newton will probably, he thinks, form the initial point for molecular mechanics. Passing from these generalities the author proceeds to the specialities of chemistry, treating of water and its compounds, of its composition, and of hydrogen.

The work is to be completed in eight parts, and will apparently extend to about 1000 pp.

Principles of General Organic Chemistry. By Prof. E. HJELT. Translated from the Author's German Edition of the Original Work by J. BISHOP TIMOLZ, Ph.D., F.C.S. London: Longmans, Green, and Co.

It is refreshing to find a general work on chemistry which has a definite purpose, and which does not compel us to raise unpleasant questions as to its possible *raison d'être*. We have, as the author remarks, systematic text-books, large and small. But as a matter of necessity they are largely filled up with the description of individual compounds, especially if new; their preparation, composition, and properties, with less regard to the

* This use of the three crucibles was suggested by Dr. W. F. Henden, Professor of Chemistry at the Dakota School of Mines.
† "Report of the Dakota School of Mines," 1888, p. 142.

meaning and the mutual bearing of all these facts. Hence the student, like the traditional Swabian knight-errant, cannot see the forest for trees. The aim of Prof. Hjelt has been to present concisely and clearly "the main points of general and theoretical organic chemistry."

We are, further, glad to note that the translator has not thought it necessary to adapt this book to the supposed needs of the British student by inserting a string of examination questions or by re-arranging the work in accordance with some "syllabus."

The author, in defining organic chemistry, makes a clear distinction between *organic* compounds, capable of synthetic reproduction, and being in general the by-products or the *rejectamenta* of life, and *organised* bodies, "the special material conductors of the vital functions," which hitherto have not been obtained artificially. The study of such bodies should, he thinks, be more correctly known as "organic chemistry." There are, of course, a number of questions which the author does not raise, but which the "chemistry of the future" will some day have to take in hand. We do not yet know why carbon lends itself so much more readily than the other elements to the formation of complicated and multifarious products, silicon making the nearest approach. The reason commonly given merely pushes the difficulty a step further away, but leaves it still unsolved. It may not be irrelevant to remark that the author, like Prof. Mendeleeff, is of opinion that petroleum is not a product of the decomposition of organic remains, but has been generated by the action of water upon ignited iron carbides in the interior of the earth, and may still be continuously produced.

The chapter on relations between colour and constitution will be found exceedingly instructive for the student.

In these days, when so much reading is demanded, great caution becomes necessary in recommending any work. But Prof. Hjelt's treatise may be advantageously taken up by any student as an explanatory accompaniment to any systematic text-book.

Law of Trade-Marks and their Registration, and Matters connected therewith, including a Chapter on Goodwill; together with the Patents, Designs, and Trade-Marks Acts 1887-88 and the Trade-Marks Rules and Instructions thereunder; Forms and Precedents, The Merchandise Marks Act, 1887, and other Statutory Enactments; the United States Statutes 1870-81 and the Rules and Forms thereunder; and the Treaty with the United States, 1877. By LEWIS BOYD SEBASTIAN, B.C.L., M.A., of Lincoln's Inn. Third Edition. London: Stevens and Sons, Limited.

This work is a useful companion-volume to Edmunds on "Patents." The subject-matter in this case, however, is one of much less interest. A patent may, and often does, involve questions which require to be decided by the chemist, the physicist, or the mechanic as the case may be. In disputes on trade-marks nothing of this kind can arise.

A valuable feature of the work before us is that it makes clear the distinction between patent, trade-mark, and copyright, which are often confounded. As we here learn, in the case of a trade-mark "the article sold is open to the world to manufacture, and the only right the plaintiff seeks is that of being able to say:—"Don't sell any goods under my mark." The property and right to protection is in the device or symbol which is invented and adopted to designate the goods to be sold, and not in the article which is manufactured or sold." A patent, while it lasts, will protect a process, whilst a trade-mark obviously cannot. We are told that the courts will discourage any attempt to prolong the term of a patent by means of a trade-mark. The insertion or retention in a trade-mark of the words "patent" or "patented," so as to indicate the protection of an existing patent, may invalidate a trade-mark.

On the other hand, "a copyright, like a patent, relates to the substance of an article, but differs in that it has reference to a literary instead of a material production." The registration of trade-marks under the Copyright Acts is shown to be useless. Still, certain quacks, "if they will permit us to call them so," have the labels for their bottles, pills, and other alleged curative appliances registered under the Copyright Acts.

On Cremation. A Discourse delivered February 13, 1890, before the Natural Science Association of Mulhouse. With an Appendix and Five Illustrations. By Prof. Dr. FRIED. GOPPELSRÖDER. Mulhouse: Wenz and Peters.

THAT Prof. Goppelsröder, as a chemist, must be a champion and advocate of cremation as *the* method for disposing of the bodies of the dead is almost a matter of course. He combats most ably the objections which have been urged against this pure and safe mode of dealing with masses of putrescent and often moribund matter. He enumerates several more or less plausible arguments which have been advanced by the adherents of interment. Foremost comes the religious scruple, which, though it has been successfully refuted by Lord Shaftesbury and Bishop Fraser, still dominates too many minds. The expression "Christian burial" still carries with it much weight, especially in a country like Britain, where we are governed by phrases and catch-words. In reality, the idea that a person can, by the incineration of his remains, forfeit all hopes of a future existence is purely materialistic.

The æsthetic side of the question is still more easily dealt with. For a couple of days after death the state of the corpse may be likened to sleep. But could the poets and novelists who dwell on this similitude ever watch the actual process of putrefaction to its end they would be simply sickened. In reality the ultimate results of incineration and of putrefaction are the same. But fire does its work rapidly and without the formation of intermediate products, always disgusting and frequently dangerous.

The third objection—the loss of manurial matter—is of little weight. Under our present system great care is taken that the remains of the dead, even a century after their deaths and after their identity has been lost sight of, shall not be again permitted to enter into the great circulation of Nature. We have heard of a contractor who was conducting alterations in a churchyard closed by authority being prosecuted for having sold to market-gardeners some loads of a soil formed in part of decayed human remains. Prof. Goppelsröder very rightly suggests that if the ash of cremated corpses is not preserved in urns it had better be given back to the soil.

The fourth objection is raised by criminal lawyers, who fear that murders may remain undiscovered if the bodies are destroyed by fire. It is certainly true that poisons have been detected in exhumed bodies, but our author shows that the longer a corpse has remained in the grave the more doubtful becomes the evidence to be obtained by a toxicological examination. What is wanted is a systematic autopsy in all cases. Such an examination would not be, on the average, more expensive or circumstantial than the perfunctory scrutiny of a coroner's jury.

The author scarcely lays sufficient weight on the pollution of soil, waters, and air, by the existence of cemeteries. The charges which Dr. Walker—"Churchyard Walker," as he was named by parochial anti-sanitarians—brought against the old City churchyards now hold good in a gradually increasing degree against our suburban cemeteries. We have visited some of these establishments in calm mild weather, and have detected odours whose nature was beyond question and beyond rational tolerance. Details we cannot give; the libels are not merely the shield but the sword of the quack and of the perpetrator of nuisances.

Prof. Goppelsroeder might have noticed a semi-reform in the disposal of the dead. We refer to the so-called "earth to earth" system of interment, which differs from that in common use merely in the circumstance that the corpse is placed, not in a firm wooden coffin, but in a slight structure of wicker-work. That this arrangement may quicken decay we admit, but that it can alter the nature of putrefaction and render it free from nuisance and danger we must deny. Hundreds and thousands of men and horses have been buried on battlefields without any coffins at all. The same has been frequently done in visitations of pestilence, but in neither case has there been any absence of offence or any impunity from danger. Most decisive is an observation made by M. Pasteur, with a quite different end in view. Some cattle attacked by splenic fever had been shot and buried three or four yards deep in the soil. Some sheep, penned afterwards over the spot, caught the very same disease. The *materies morbi*—whether it be considered as organised or unorganised—had not been destroyed by burial in immediate contact with the soil, but had been conveyed up to the surface by the earth-worms. When once there the flies would effect its distribution and even its inoculation into man and beast. In case of visitations of the plague cremation is, as we here learn, legally compulsory in Russia. A similar law, we believe, is in force in Brazil in epidemics of yellow fever.

We cannot conclude this short notice of a valuable little work without acknowledging the service rendered by Herr Fr. Siemens to the cause of cremation by the application of his regenerative furnace.

The Colour Reactions of the Carbon Compounds. For Chemical, Physiological, Micro-chemical, Botanical, Medical, and Pharmaceutical Investigations. Compiled by Dr. EMIL NICKEL. Second Edition, Revised and Enlarged. Berlin: W. H. Peters.

THE author tells us in his preface that the investigations here made public have sprung from a study of the chemistry of lignification. It appeared to him desirable to submit the entire sphere of the coloured reactions of the hydrocarbons to a thorough revision, and to test the customary reagents as to their trustworthiness. By so doing he has conferred a great boon, not merely on students of certain departments of chemistry, but upon biologists and microscopists. He first takes up the coloured reactions with an aromatic character, those obtained with the co-operation of nitrous acid and its derivatives (exclusive of the production of the azo-colours). Here he particularly discusses the colour-reactions with the reagents of Millon, Hoffmann, Plügge, and Liebermann and certain new reactions with new reagents. The above reactions he proposes to classify as the nitroso-reactions. Then follow the reactions with nitric acid, that with xantho-proteic acid, Scherer's inosite test, and Serdel's reaction. Next we have the colour-reactions, comprising the formation of the azo-colours, such as Weselsky's reaction and its extensions, and Ehrlich's reactions with paradiabenzol sulpho acid.

Chapter IV. treats of the colour reactions which depend on the formation of triphenylmethane dyes and analogous compounds.

Next we come to coloured reactions in which ferric salts and chromates are concerned. Here the caution is given that these reactions are not necessarily specific, and that they, consequently do not at once prove the presence of tannin or its modifications.

In the second part the author considers colour-reactions in which nuclei are not concerned and those with an unknown character. Here belong the colour reactions with which the cyanogen group is involved, those in which murexide and its analogues are formed, and those in which inorganic colouring matters are produced. Instances of this class are given by the reagents of Nessler and Froehde.

This little treatise will be the means of preventing many confused or contradictory results, or, we might venture to say, much bad work.

Catalogue of Minerals For Sale by G. L. English & Co. Chestnut Street, Philadelphia, and Broadway, New York. Fifteenth Edition.

THE demand for mineralogical specimens, whether for the cabinet or as subjects for chemical, &c., examination is now sufficiently extensive to make it worth the while of a respectable firm to take up this subject as a speciality.

Messrs. English & Co. offer a very extensive collection of minerals from all parts of the world, and especially American rarities, some of them exceedingly interesting.

Among the illustrations the figure of Almandite garnets embedded in mica-schist may be mentioned as especially beautiful.

CORRESPONDENCE.

OZONE PHOSPHORESCENCE.

To the Editor of the Chemical News.

SIR,—I have been especially interested by Mr. Ernst Fabrig's paper on this subject in your last issue, for in January of this year I had an opportunity of witnessing the experiment, and I can bear testimony to the fact of the production of a distinct glow or phosphorescence on the addition of distilled water, previously shaken with strongly ozonised oxygen, to about a litre of Thames water obtained by myself from near Blackfriars Pier. The experiment was performed in a quite dark room, under the close observation of fourteen or fifteen persons standing around, all of whom, I believe, saw the phosphorescence. The phenomenon impressed me very much, and I have felt it a misfortune that pressure of work has hitherto prevented me from making any experiments in this direction worth describing.

I may mention that a statement was made, on the occasion to which I have referred, that the phosphorescence is not produced when an ozone solution is added to sterilised distilled water, and that water of fair organic purity will only yield a very faint glow: the explanation suggested being that the phosphorescence is the result of the action of ozone upon the micro-organisms—and perhaps, also, the dead organic matter—present in impure water. I notice, however, that some of Mr. Fabrig's observations scarcely tend to confirm this opinion.—I am, &c.,

EDWY GODWIN CLAYTON, F.I.C., F.C.S.

Certain Applications of Thermo-Chemistry to the Study of the Constitution of the Organic Alkalies.—

A. Colson.—In one and the same group the molecular heat of neutralisation falls gradually from the primary to the tertiary amine, the sum of the solution-heat and of the neutralisation-heat, or total heat, remaining constant. The molecular heat of neutralisation for one and the same acid increases with the weight of the mol. in the primary amines of the fatty series. If we call *strong bases* those which exactly neutralise acids, and a small excess of which turns tincture of litmus to a blue, and *weak bases* those which do not fulfil these conditions, we remark that the non-saturated bases of the fatty series are strong bases, but their total heat and their solution-heat are strikingly rendered. If the amidogen group is directly joined to the aromatic nucleus experience shows that the base becomes feeble. Nicotin, which is bibasic, is a strong base by one of its basicities and a feeble base by the other.—*Revue Generale des Sciences Pures et Appliquees*, Vol. i., No. 12.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 2, July 15, 1890.

The Laws of Berthollet.—Albert Colson.—The bases may be subdivided into categories of the same order independently of their nature. Keeping in view the two principal groups, the one comprising bases strong enough to precipitate magnesium chloride, the other composed of feeble bases, unable to displace magnesia, we find that a dissolved salt formed by a strong base is not decomposed by a weak base, whilst a salt constituted by a weak base is decomposed by a strong base, whatever may be the solubility and the nature of the two bases if the salt which tends to be formed is soluble.

Researches on the Double Rhodium Nitrites.—E. Leidé.—The author has re-examined the reactions of the alkaline nitrites as given by Claus, Lang, and Gibbs. He finds errors and contradictions in their memoirs, and has repeated their work with especial reference to the rhodium and potassium nitrites, and the corresponding double sodium and ammonium salts, and the rhodium barium nitrite. The properties of these double salts are valuable in analysis; especially those of the double rhodium-potassium salt may be utilised for extracting rhodium in a state of purity, separating it from the other platinum metals, and determining it in its combinations. These points will be developed in a future communication.

Certain Compounds of Camphor with the Phenols and their Derivatives.—E. Léger.—The author has demonstrated that camphor produces with the phenols two combinations, which their great instability and the ease with which they are split up by heat, by solvents, and alkalis have caused to be mistaken for mere mixtures. He establishes that camphor and the phenols unite in simple proportions to form the bodies in question. These bodies when solidified by heat give crystals of which the portions formed successively have always the same composition. The introduction of the phenols into the alcoholic solutions of camphor diminish its rotatory power by nearly the half.

On Certain New Derivatives of β -Pyrazol. A Contribution to the Study of the Nitric Ethers.—M. Maquenne.—This paper is not adapted for useful abridgment.

Colouring Reagents of the Fundamental Substances of the Vegetable Membrane.—L. Mangin.—See p. 52.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 10.

Reclamation by MM. Vincent and Delachanal on the Determination of the Acetone contained in the Methylenes.—In reply to the claim of M. Messenger based on publication in the Berlin *Berichte*, November 28, 1888, the authors show that their process was published in 1882.

Extraction of Raffinose from Treacles.—L. Lindet.—The author finds indirect proof of the existence of compounds intermediate between saccharose and raffinose.

Chloro-Derivatives of the Amylamines.—A. Berg. This paper is not adapted for useful abstraction.

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PRINCIPLES OF
GENERAL ORGANIC CHEMISTRY.

By PROFESSOR E. HJELT,
of Helsingfors.

Translated from the German by J. BISHOP TINGLE,
Ph.D., Assistant in the Laboratory of the Heriot
Watt College, Edinburgh.

In this work the fundamental theories of organic chemistry are presented in a clear and concise form, and their application is fully illustrated by examples. The relations between the constitution of compounds and their chemical and physical properties are prominently exhibited. A considerable number of general reactions are discussed and explained; in all cases these are classified according to the results; for instance, reactions involving oxidation are grouped together, and examples are given of the effects of oxidation on different classes of compounds: a lucid account is also given of the special application of particular oxidizing agents.

LONDON: LONGMANS, GREEN, AND CO.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that

ARTHUR GEORGE GREEN, of the firm of Brooke, Simpson, and Spiller, Limited, of Hackney Wick, County Middlesex, has applied for leave to amend the Specification of Letters Patent No. 15,449 of 1886, for "Improvements in the preparation of a Beta-naphthylamine Sulphonic Acid and of colouring matters therefrom."

Particulars of the proposed amendment were set forth in the Illustrated Official Journal (Patents) issued on the 23rd July, 1890.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed)

H. READER LACK,
Comptroller-General.

THE LONDON HOSPITAL MEDICAL

COLLEGE.—The WINTER SESSION will commence on Wednesday, October 1st.

The Hospital, which is the largest general hospital in the kingdom, contains nearly 800 beds, all in constant use. There are wards for accidents, surgical and medical cases, diseases of women and children, and ophthalmic cases. Special departments for diseases of the eye, ear, throat, skin and teeth, and for cancer, tumours, diseases of the bladder, piles and fistula. Number of in-patients last year, 905; out-patients, 109,899; accidents, 11,400.

Surgical operations daily.
APPOINTMENTS.—Resident accoucheur, house physician, house surgeons, &c. Forty of these appointments are made annually. Numerous dressers, clinical clerks, post-mortem clerks, and maternity assistants are appointed every three months. All appointments are free. Holders of resident appointments are also provided free board. Two Entrance Science Scholarships, value £75 and £50, and two Buxton Scholarships, value £30 and £20, will be offered for competition at the end of September to new Students. Sixteen other Scholarships and prizes are given annually.

The London Hospital is now in direct communication with all parts of the metropolis. The Metropolitan District, and other railways have stations within a minute's walk of the Hospital and College.

For further information apply, personally or by letter, to—

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PATENTS.

MR. J. C. STEVENS will Sell by Auction at his Great Rooms, 38, King Street, Covent Garden, on Friday, August 15, the following Patents, with Specifications and Drawings:—

1. Patent for Improvement in the Manufacture of Sulphuric Acid.
2. Patent for Improvement in the Distillation of Tar in the Manufacture of Oil, Illuminating and Heating Gas.
3. Patent for Improvement in the Purification of Sewage and making Alkali and Cement therefrom.
4. Patent for Improvements in the Manufacture of Soda by the Ammonia Process.
5. Patent for Improvement in the Construction of Retorts for Destructive Distillation of Shale and other Substances for Extracting Oil.
6. Patent for Improvements in the Manufacture of Sulphate of Soda and Bleach.

Specifications and drawings on view after 2 p.m. the day prior, and morning of sale.

THE CHEMICAL NEWS.

VOL. LXII. No. 1602.

THE OCCURRENCE OF CANE SUGAR IN THE SWEET POTATO.

By W. E. STONE.

THE sweet potato is said by De Candolle to be "sugary as well as farinaceous." This "sugary" nature undoubtedly constitutes one of its most attractive qualities as an edible, although it is also to a high degree farinaceous. The analytical data which I have been able to collect are scattering and somewhat at variance, while with one or two exceptions they were obtained many years ago, by methods which would now hardly be regarded as accurate.

One analysis by Henry is as follows:—(only data relating to the carbohydrates are cited.)

Water	73.1 per cent.
Starch	13.3 "
Sugar	3.3 "

Another analysis by Johnson is:—

Starch, 40.9	per cent.
Gums, 1.4	"
Sugar, 19.7	"

These percentages undoubtedly relate to dry matter.

In "Ure's Dictionary" an analysis is also cited as follows:—

Water	74.3 per cent.
Starch	15.1 "

The absence of any mention of sugar in this is noticeable. Analysis made at the department of agriculture from partially dried samples gave:—

Starch	65.29 per cent.
Sugar	14.83 "

Some more recent analyses are, one made at the Connecticut experiment station:—

Water	73.89 per cent.
Carbohydrates	23.60 "

and at the New York experiment station:—

Water	74.38 per cent.
Nitrogen-free extract	17.98 "

The ambiguous term "sugar" used in these data gives us no clue to the specific nature of the carbohydrates indicated thereby. In only one place have I found a reference to the character of this sugar, viz., in connection with the analysis made at the United States Department of Agriculture. Here it is stated that the potato meal, on mixing with cold water, contained no glucose, but after heating to boiling acquired the power of reducing Fehling's solution. The original form of this reducing sugar was stated to be sucrose, for which, however, the above described behaviour cannot serve as convincing proof. In the complicated mixture existing in the watery extract of vegetable tissues, reducing compounds may arise from quite other sources than sucrose at boiling temperature. So also in the quantitative inversion of such an extract, with strong acids, many other substances besides sucrose are subjected to hydrolysis, and may give similar results. It is recognised at present that the one

conclusive proof of the occurrence of a specific saccharine compound consists in its isolation in a pure state, and the application of characteristic reactions, chief of which is the determination of its *specific rotation*. To this end samples of two well-known varieties, Southern queen and American red, were taken in hand. The date was fully three months after harvest, but the potatoes were still fresh and sound. As bearing upon this point, the following determinations were made:—

	Specific gravity.	Moisture.	Dry matter.
Southern queen ..	1.017 ..	59.37 ..	40.63
American red ..	1.059 ..	61.22 ..	38.78

The flesh of both sorts showed most intense colouration with iodine, indicating large quantities of starch. A watery extract from the grated flesh of the Southern queen samples had no effect upon Fehling's solution, even after maceration for several hours in the cold. A similar preparation from the American red gave only a slight reduction. In both cases the watery extract was sweet to the taste. Often in the course of investigation, similar tests were made with other samples, and always with the same results, *i.e.*, often without reduction of Fehling's solution and never with anything more than a slight reaction, from which I conclude that under ordinary conditions the sweet potato contains no reducing sugar; or at least only slight traces of the same.

About 300 grms. of the finely grated pulp of each variety were digested at boiling temperature during three hours with 600 c.c. of strong alcohol, in flasks connected with return condensers. The alcoholic extracts thus obtained were filtered, and the filtrates evaporated to the consistency of thin syrup. Both products were very sweet and somewhat dark coloured; that from the American red was reddish coloured, due to matters extracted from the dark red skin of this variety. These residues were boiled with four to five volumes of strong alcohol, and on cooling a thick dark coloured gummy syrup settled to the sides and bottoms of the flasks. The clear alcoholic solutions were decanted and treated with animal charcoal, whereby much of the colouring matter was removed. After filtering from the charcoal, the alcoholic solutions were evaporated and left to crystallise. That from the Southern queen soon became quite solid from the formation of sugar crystals. The syrup obtained from the American red, however, contained several transparent oily globules, and refused to crystallise. This oily substance was soluble in alcohol, and had accompanied the syrup through all the refining operations. On treatment with water, however, it was precipitated as a white flocculent mass. By filtration and evaporation of this watery solution, a syrup was obtained which also soon crystallised.

The crystalline products thus obtained from the two varieties were apparently identical in their nature. They were united in one portion and purified by repeated recrystallisation from alcohol and water. The ultimate product was crystalline, pure white, and sweet to the taste.

A small portion was placed in a flask with compressed yeast, and in the course of a few hours a distinct fermentation had followed. The gas evolved was collected in a eudiometer tube, and proved to be carbon dioxide. The sugar did not directly reduce Fehling's solution, but after treatment in solution with a few drops of hydrochloric acid, showed a strong reducing action.

To determine the specific rotation, 4.1334 grs. were dissolved in water and made up to a volume of 50 c.c. This solution was polarised in the Laurent's polariscope made by Schmidt and Haensch of Berlin, and in a tube of 200 m.m. length showed a dextro-rotation of 10.87°. From these data the specific rotation is calculated to be (α)_D=65.7°, which agrees practically with that for cane sugar as determined by Tollens.*

* "Handbuch der Kohlenhydrate," p. 124.

* Watts' "Chemical Dictionary," p. 250.

† Journal Royal Agricultural Society, xiii., p. 522.

‡ Reference in Rept. Dept. Agriculture Report, 1869, p. 76.

§ Ibid.

¶ Rept. Conn. Experiment Station, 1878, p. 78.

¶ Seventh Annual Rept. New York Experiment Station, p. 243.

There seems no doubt, therefore, that the sugar of the sweet potato is sucrose.

Several months were occupied in obtaining these results, but early in the investigation, after ascertaining that the sugar present was non-reducing, an attempt was made to determine the same quantitatively by means of polarisation. Two portions of the freshly grated pulp of the American red were extracted with strong alcohol, during two or three hours, in a Soxhlet apparatus, the clear extract made up to 100 c.c. and polarised in a 200 m.m. tube in the above-mentioned Laurent's apparatus. The results were as follows:—

1. 35.30 grs. of pulp extracted and diluted to 100 c.c. showed a dextro-rotation of $4.5^\circ = 2.09$ per cent sucrose.

2. 34.95 grs. of pulp in the same proportion as above, showed a dextro-rotation of $4.46^\circ = 2.10$ per cent sucrose.

A similar determination with the Southern queen gave the following results:—

3. 35.31 grs. of pulp in the proportions already given gave a dextro-rotation of $3.17^\circ = 1.44$ per cent sucrose.

These results fall somewhat below those already cited at the beginning of this paper, and while considerable variation undoubtedly exists between different varieties, and even between samples of the same variety grown in different localities, yet I believe the methods of polarisation may be safely applied to the quantitative determination of the sucrose existing here. The data quoted were undoubtedly obtained by methods of inversion, and if so would naturally be too high. On the other hand, as we have seen, the amount of reducing sugar (glucose) present in the fresh potato is minimal, if not entirely wanting, and by no means sufficient to produce an appreciable diminution of the reading produced by sucrose present. From data obtained, therefore, it would appear that the percentage of sucrose present in the varieties named is from one and a-half to two per cent.

If we take a sweet potato, the flesh of which has been previously found to be quite free from reducing substances, bake it in the ordinary domestic fashion, crush it and macerate the mass with cold water, the extract thus obtained will reduce Fehling's solution strongly. The temperature applied in baking has produced inversion among the carbohydrates originally present.

To a watery extract obtained as above, two volumes of strong alcohol were added, by which a voluminous, flocculent, white precipitate was thrown down. This was filtered, and the filtrate evaporated to a syrup, which was of a brownish yellow colour, very sweet, and still retained its reducing power.

The precipitate, which was at first somewhat sticky and gummy, by repeated washings with strong alcohol and ether, became pulverulent and no longer deliquescent on exposure to the air. This substance was readily soluble in water, but the solution was not sweet to the taste. With iodine solution a most intense violet or purple colour was produced, which, however, was quite distinct from the ordinary starch reaction. The solution reduced Fehling's solution after heating, but the appearance was different from the normal glucose reduction. A solution of 1623 grms. in 100 c.c. of water produced in a 100 m.m. tube a dextro-rotation of 2.86° , from which the specific rotation $(\alpha)_D = 176.3^\circ$ may be calculated. This substance corresponds in its behaviour to some of the compounds occurring in the transition from starch to dextrine or, eventually, dextrose. The specific rotation is too low for mere soluble starch, which according to Brown and Morris is $(\alpha)_D = 194.8^\circ$, and approaches more nearly that of malto-dextrose $[(\alpha)_D = 174.5^\circ]$. The latter, however, does not give the iodine reaction. The substance in question was undoubtedly a form of soluble starch or amylodextrine, produced by the action of heat upon the starch of the potato.

The syrup obtained by evaporation of the watery extract from which the soluble starch had been precipitated, was of a very sweet and altogether agreeable taste.

It reduced Fehling's solution strongly. In spite of attempts at purification and decolourisation, it remained somewhat dark coloured and refused to crystallise. After standing some weeks, it was still perfectly clear and amber-like in appearance. Its behaviour indicated that while some of the original cane sugar may have been present, it was also accompanied by a considerable quantity of invert sugar. Treatment of a portion of this syrup with phenylhydrazin chloride, according to the prescribed method,* gave an abundance of the characteristic yellow product which in this case seemed to be the phenyl-glucosazon. This, after re-crystallisation from alcohol and desiccation, melted at 200° to 204° C., practically agreeing with the number (204° to 205° C.) for pure glucose. The syrup was therefore an impure glucose resulting from the inversion of the original sucrose of the potato.

Briefly stated the results of the inquiry are:—

The saccharine substance of the sweet potato exists chiefly, if not entirely, in the form of sucrose.

The use of the polariscope in the quantitative determination of the same seems possible. Such determinations showed one and a-half to two per cent of sucrose in the fresh potatoes.

The temperature of cooking (baking) inverts the sucrose, and converts more or less of the starch into a soluble form.

A part of this investigation was made at the laboratory of the Tennessee Experiment Station, the remainder at Purdue University.

NEW PROCESS FOR THE TITRATION OF ALDEHYD BY MEANS OF CHROMIC ACID.

By R. BOURCART.

THE process is substantially the same as that described for alcohol. 1 mol. aldehyd requires $\frac{1}{2}$ mol. bichromate for conversion into acetic acid. 1.2442 grms. of pure paraldehyd is made up to a solution of 100 c.c. with water. The solution of bichromate contains exactly 10 grms. of the salt to 1 litre, and a hyposulphite solution of 24 grms. per litre, of which 104.2 c.c. correspond to 100 c.c. of the bichromate solution. The determination is carried out as for alcohol, heating for three hours to 100° . The quantities taken were 10 c.c. solution of paraldehyd, 20 c.c. sulphuric acid of 10 vol. per cent, 50 c.c. of the bichromate solution, and 20 c.c. potassium iodide of 10 per cent.—*Soc. Indust. de Mulhouse and Chemiker Zeitung.*

ON A NEW PROCESS FOR DETERMINING THE MINERAL MATTER IN SUGARS BY MEANS OF BENZOIC ACID.

By E. BOYER.

THE direct incineration of sugars for determining the inorganic matter is a long and delicate operation, for which there has been substituted in industrial analysis the empirical procedure indicated by Scheibler, which consists in incinerating a known weight of sugar in presence of pure concentrated sulphuric acid until a perfectly white ash is obtained. It is generally assumed that if we deduct the tenth of the weight of the sulphated ash the figure remaining will represent the weight of the

* One part of the sugar or syrup, two parts phenylhydrazin chloride, three parts sodium acetate, and 20 parts water are warmed together in a water bath to 70° to 80° C., whereby fine yellow crystals are gradually formed. This compound, $C_{12}H_{16}N_4O_4$, has a characteristic melting-point accordingly as it is derived from one or the other of the sugars.

mineral matter. Several chemists, especially MM. Aimé Girard and Violette hold that this correction is insufficient, the ash of sugar consisting chiefly of alkaline carbonates and chlorides, and they propose to deduct 2-roths of the gross weight in order to obtain the real mineral matter of sugars.

We see, in fact, by a calculation of the equivalents, that this latter correction approaches the reality.

The process which the subject of this paper embraces has the advantage of dispensing with any correction, since it gives directly the mineral matter of sugar in its natural state. It consists in effecting the carbonisation of the sugar in presence of a volatile acid, benzoic acid. To facilitate the mixture of this acid with the sugar it is preferably employed in solution, and as it is but sparingly soluble in water, alcohol at 90 per cent is used as solvent, 100 c.c. to 25 grms. benzoic acid.

He weighs into a platinum capsule 5 grms., which are moistened with 1 c.c. distilled water; the capsule is gently heated over a Bunsen burner so as to caramelise the sugar without charring it, so that all the carbon may be ultimately formed in presence of benzoic acid. The addition of water renders this manipulation easy. He then adds 2 c.c. of the alcoholic benzoic solution, say 0.5 gm. of the acid, and evaporates on the sand-bath, heating at first gently until the alcohol is entirely driven off, and then raising the heat to effect the carbonisation.

The decomposing benzoic acid gives off abundant vapours, which swell up the sugary matter, especially if we take the precaution of giving the capsule a rotatory movement. The heating is continued until all the benzoic acid is volatilised.

The carbon obtained is bulky and of a brilliant black. To effect the combustion the capsule is put at the entrance of a muffle furnace heated to dull redness. The incineration is complete in half-an-hour, and the ash obtained is white and bulky.

The capsule is weighed rapidly after cooling in order to avoid the absorption of moisture by the alkaline carbonates.

The weight obtained represents the mineral matter in 5 grms. sugar. Ammonium benzoate may be used instead of benzoic acid, but whichever is taken we must first ascertain that it leaves no residue in the conditions of the analysis.

The results given by this method are accordant, and justify the deduction of 2-roths from the weight of the sulphated ash to obtain the real mineral matters of sugars of the first and second quality. Subjoined are some determinations compared with the results of the sulphuric determinations corrected by the successive deduction of 1-roth and 2-roths:—

Kind of Sugar.	Benzoic Incineration.	Sulphuric Incineration.		
		Uncorrected.	1-roth corrected.	2-roths corrected.
Blank experiment ..	0.06	0.08	0.07	0.06
First quality ..	0.73	0.90	0.81	0.72
Second ..	0.94	1.18	1.06	0.94
Mixture ..	1.81	2.25	2.03	1.80

—Comptes Rendus, July 21, 1890, p. 190.

RECOVERY OF ABSORBED MORPHINE FROM THE URINE, THE BLOOD, AND THE TISSUES.*

By THEODORE G. WORMLEY, M.D., LL.D.,
Professor of Chemistry and Toxicology, Medical Department,
University of Pennsylvania.

Historical.—Of all the ordinary poisons there is none that has more frequently been attended with failure to recover it from the body, both in poisoning of the human

subject and in experiments on animals, than the alkaloid morphine. These failures have occurred even when the quantity taken or administered was very large, and all the attending circumstances apparently the most favourable for its recovery. Indeed, in the numerous experiments thus far made upon animals, the results have been negative, save in a few instances.

Among the earlier observers, Dr. Christison ("On Poisons," Amer. Ed., p. 537) failed to detect morphine in the contents of the stomach of a young woman who died in five hours after taking two ounces of laudanum; and in another instance the contents of the stomach, withdrawn four hours after two ounces of laudanum had been taken, failed to furnish satisfactory evidence of the presence of the poison.

M. Dublanc (*Archives Gen.*, i., 150) sought in vain for morphine in the blood and urine of animals killed by it. And M. Lassaigue (*Ann. de Chim. et de Phys.*, xxv., 102) could not detect the alkaloid in the blood drawn from a dog twelve hours after thirty-six grains of the acetate were injected into the crural vein; nor, again (*Four. de Chim. Med.*, 1841, 488), in the liver or the blood of a dog poisoned with eight ounces of Sydenham's laudanum.

Orfila ("Traité des Poisons ou Toxicologie," trois. Ed., ii., 58) failed to find the poison in the blood of three dogs that had been given respectively twelve, fifteen, and eighteen grains morphine acetate, and found it in only one instance in the urine.

Bouchardat (*Bull. Gen. de Ther.*, Dec., 1861) believed he had found the alkaloid in the urine of a person who had taken 0.05 gm.; and Lefort (*Four. de Chim.*, xi., 93, 1861) concluded that it was eliminated by the urine. But the tests relied upon by these observers—iodine in potassium iodide by the former, and iodic acid by the latter—have no positive value.

Dr. Taylor ("On Poisons," London, 1875, 34) mentions two cases, one in his own practice, in each of which one grain of morphine hydrochloride had been taken, and death took place in ten and thirteen hours respectively; but no trace of morphine could be detected in the stomach in either case.

Dr. Ebertz (*Ann. d'Hyg.*, 1875, July, 220) failed to find a trace of the poison in any part of the body of a woman who had taken 0.25 gm. (nearly four grains) of a salt of morphine, and died from its effects within fifty minutes afterward.

Dr. Ogston ("Lectures on Medical Jurisprudence," 1878, 567) records a case in which nine or ten grains of morphine hydrochloride caused death within a few hours, and none of the poison had been ejected and no remedy applied. A most searching examination, by himself and Professor Gregory failed to detect any trace of morphine in the alimentary canal or elsewhere.

In a fatal case of laudanum poisoning recorded by Dr. Tidy ("Forensic Medicine," 1877, 376), repeated analyses of the contents of the stomach failed to reveal the presence of a trace of either meconic acid or of morphine.

In experiments upon three rabbits, Erdmann (*Annal. d. Chem. u. Pharm.*, Bd. 122, 360, 1862) found the poison in the first, in the stomach; in the second, only traces in the urine; and in the third, only traces in the blood, none being found in the urine, brain, or spinal cord. He concluded that morphine was decomposed in the system.

Cloëta (*Virchow's Archiv.*, xxxv., p. 376, 1866) examined, by Erdmann's method, the urine of a patient who had taken for some time daily six to seven grains morphine acetate, but failed to find a trace of the poison.

In a case of morphine poisoning, Dr. Kreyssig ("Inaugural Dissertation," Leipzig, 1856; quoted by Landsberg) found the poison in the vomited matters by the iron test, but failed to find a trace either in the blood or urine. Prof. Maschka (*Prager Vierteljahr.*, Bd. 66, p. 65, 1860) reports a similar case in which none of the poison was found in the stomach.

* From the *University Medical Magazine*.

Prof. L. A. Buchner (*Neues Repert. f. Pharm.*, Bd. 16, p. 43, 1867) relates the case of a child quickly killed by three doses of morphine acetate of two grains each, and he failed to find any evidence of morphine either in the contents of the stomach or alimentary canal. And in another case, in which a child quickly died from the effect of extract of poppies, similar negative results were obtained.

H. Köhler (*Schmidt's Jahrb.*, Bd. 141, p. 21, 1869) states that the recovery of morphine from bodies by the known methods more frequently fails than succeeds. Prof. Guy ("Forensic Medicine," p. 518, 1881) remarks that it is now well understood that in cases of poisoning with opium the best methods of analysis will often fail to yield any evidence whatever of the presence of the poison in the contents of the stomach.

Gscheidl (*Arbeiten aus dem Physiol. Laborat.*, Würzburg, Bd. 32, 1869) says that morphine injected into the jugular vein of rabbits may be found in the urine; but this may be due to the great amount administered.

Kauzmann (*Zeitsch. f. Analyt. Chemie*, viii., pp. 103, 243, 1869) found that morphine might be recovered unchanged from the stomach, feces, the blood, and urine. He employed the Usler-Erdmann method.

E. Vogt (*Archiv. der Pharmacie*, Bd. 207, p. 23, 1875) failed to find morphine in the urine for twenty-four hours of an old man who took daily large quantities of the drug, but he found it in the feces. In like manner, Bornträger (*Archiv. der Pharmacie*, Bd. 217, p. 119, 1880) failed to find the poison in the urine of a person who took daily 0.5 to 1.0 gm. subcutaneously.

Jacques ("Localisation des Alcaloides dans le Foie," Thèse Bruxelles, 1880; cited by Landsberg) relates the case of a person, sixty years old, who took for five years daily 1.3 grms. morphine in solution, and in addition every second day 2.0 grms. subcutaneously, yet he failed to find the alkaloid in the urine, but found it in large quantity in the feces collected for three days.

Dr. W. Eliassow ("Inaugural Dissertation, Königsberg," 1882) examined with negative results the urine of a person who took daily 0.14 gm. of a salt of morphine. So, also, R. Burkart (*Volkmann's Sammlung Klinischen Vorträge*, N. 238) failed to find it in the urine of persons who took morphine in large doses; yet on adding directly 0.002 gm. morphine to 50 c.c. urine, he readily obtained evidence of its presence.

E. Landsberg (*Pfäuger's Archiv. f. Physiologie*, Bd. 23, p. 425, 1880) injected subcutaneously into three dogs quantities of morphine hydrochloride, varying from 0.2 to 0.4 gm. The urine from these animals failed to show the presence of morphine. In another case 1.0 gm. of the morphine salt was injected; the next day 0.5 gm., and on the third day 1.0 gm. Four hours after the last dose the animal was killed, and 170 c.c. urine collected. But no morphine was found in this fluid, nor in the brain, medulla oblongata, or in the liver. In another case 2.7 grms. of this salt were injected in divided doses over several days; 130 c.c. of urine and the blood were then examined, but with negative results. One gm. of the salt was administered, in two portions, by the stomach. Again the urine failed to show the presence of the poison, but it was readily obtained from the feces. From these and other experiments Landsberg concluded that morphine undergoes decomposition in the system.

R. Schneider (*Jahresbericht für Tierchemie*, 1884, p. 236), under the action of Froehde's reagent, found morphine in the urine of three persons who took daily from 0.02 to 0.36 gm. morphine acetate, partly internally and partly by subcutaneous injection.

Dr. J. Donath (*Archiv. f. d. ges. Physiologie*, Bd. 38, p. 541, 1886) examined the urine of a patient who had for five years taken large doses of morphine subcutaneously, and during forty-eight hours had employed 0.36 gm. of the alkaloid. Two litres of urine collected during the two following days, examined by Landsberg's method, failed to reveal the presence of a trace of mor-

phine. The urine of this patient was examined subsequently a second and a third time, with like negative results. In another case, in which the patient was using subcutaneously 0.75 gm. of a morphine salt daily, 1200 c.c. of the urine failed to give any positive evidence of the presence of morphine. In a third case, in which 1.5 grms. were injected during forty-eight hours, not a trace of morphine was found in 2.5 litres of urine. From these examinations Dr. Donath concludes that morphine entirely disappears in the animal organism, and is not converted into any product that responds to the tests for morphine.

With the cases now cited may be mentioned the results of the writer's ("Micro-Chemistry of Poisons," 867, 502) own investigations, made some year's since, in which the blood from eight different cats and dogs poisoned by opium gave little or no evidence whatever of the presence of the poison, save in one instance, in which two grains of morphine and two ounces of laudanum had been administered.

Methods of Analysis.—In the early history of this subject about the only method known for the recovery of morphine and the alkaloids in general, from complex mixtures and the tissues, consisted in extracting the finely divided solids by water acidulated with acetic acid, evaporating the filtered liquid, and extracting the residue with alcohol. In the further purification of the extract, acetate of lead was used to separate foreign organic matter, and the alkaloid was finally precipitated by sodium carbonate.

After this general method M. Lassaigne (*Ann. de Chim. et de Phys.*, xxv., 102) recovered morphine when the quantity was not less than two grains in eight ounces of the complex mixture.

About the only tests then known for the recognition of morphine were the iron and the nitric and iodic acid tests.

In 1851 Professor Stas (*Bull. de l'Académie de Médecine*, ix., 304), of Brussels, proposed a general method for the recovery of the alkaloids from organic mixtures, based upon the fact that these bodies in the free state are, for the most part, more or less soluble in ether. This method consists essentially of first extracting the alkaloid in the form of a salt, from the complex mixture, by acidulated alcohol, evaporating the alcoholic extract to dryness, dissolving the residue in water, and treating this solution with an alkali to set free the alkaloid. The alkaline liquid is then agitated with several volumes of ether, which will extract the eliminated alkaloid, and, on evaporation, leave it in a more or less pure state.

Professor Otto (*Ann. Chem. Pharm.*, 100, 44, 1856) proposed to modify this method by first agitating the acidulated liquid, before the addition of an alkali, with ether for the purpose of removing certain foreign matters. The aqueous liquid, after decanting the ether, is then rendered alkaline and again extracted by ether. This proved to be an important modification of Stas's original method.

Although the method of Stas has proved of the greatest importance for the recovery of the alkaloids in general, yet it has only a limited value for the recovery of morphine, since this alkaloid requires about 7000 times its weight of ether for solution. Nor is chloroform, as first advised by Rodgers and Girdwood (*Lancet*, London, June, 1856, 718) for the recovery of strychnine, well fitted for this purpose, since morphine is about as insoluble in this liquid as in ether.

For the recovery of the alkaloids in general, but more especially for the extraction of morphine, Usler and Erdmann (*Annal. d. Chemie. und Pharmacie*, 120, p. 121) in 1861, proposed the use of amyl alcohol, in which morphine is rather freely soluble. This liquid being immiscible with water, the principle and method of application is the same as in the process of Stas.

Soon after the introduction of this method for the recovery of morphine, Froehde (*Zeitschr. Anal. Chem.*, v.,

p. 214, 1866) made the important observation that morphine and its salts in the solid state, when brought in contact with a drop of concentrated sulphuric acid holding a little molybdic acid in solution, gives rise to a beautiful purple or crimson colouration. This reaction has proved of great value for the detection of morphine, since, when properly observed, it is less open to fallacy than most of the other tests, and surpasses them all in delicacy of reaction.

(To be continued).

ON THE CHEMICAL COMPOSITION OF THE OILS OF WINTERGREEN AND BIRCH, AND THE CHARACTERS OF THE SYNTHETIC OIL OF WINTERGREEN.

By Prof. Dr. FREDERICK B. POWER,
University of Wisconsin.

In the *American Journal of Pharmacy*, 1889, p. 398, there appeared a "Contribution from the Chemical Laboratory of the Philadelphia College of Pharmacy," entitled "The Oils of Wintergreen and Birch," by Henry Trimble and Hermann J. M. Schroeter, in which the authors introduce the subject of their investigation by the following statement:

"The history of these oils has recently been written by Dr. E. R. Squibb (*Ephemeris*, Oct., 1887, p. 951), and the papers there referred to from the first in 1842 by Professor Procter to the last in 1884 by Mr. H. P. Pettigrew, can all be found in the *American Journal of Pharmacy*."

Although this carefully worded statement is literally true, I may call attention to the fact that all the literature concerning these two oils is not contained in the journal cited. In August, 1888, a paper was read by me before the Chemical Section of the American Association for the Advancement of Science, Cleveland Meeting, "On the Constituents of Wintergreen Leaves" (Power and Werbke), which was subsequently printed in abstract in the *Proceedings* of the above Association, p. 124, and in full in the *Pharmaceut. Rundschau*, Sept., 1888, p. 208, as also in the *London Pharm. Journal*, Nov. 3, 1888, p. 349, and in abstract in the *Bericht* of Messrs. Schimmel and Co., Leipzig, Oct., 1888, p. 40, and in some other periodicals. In this paper, in connection with some observations on the oils in question, and other constituents of wintergreen leaves, I also took occasion to suggest that the synthetic oil of wintergreen might properly be recognised in the next revision of the U.S. Pharmacopœia.

Since Messrs. Trimble and Schroeter have omitted any direct reference to my previous paper on this subject, it would be charitable to presume that they were unaware of its publication, but from some of the statements in their article it would not appear probable that such was the case, and having thus directed attention to this matter it may be passed without further comment.

The statements made by these gentlemen in their recent publication concerning the oils of wintergreen and birch are, however, so remarkable in many respects that I have taken the liberty of reviewing the results and conclusions of their investigation; and although good and sufficient reasons might be presented for inferring *a priori* the incorrectness of many of their statements, yet in the interest of scientific truth, and in order that the critical remarks which I desire to make may be as thoroughly substantiated as possible, I have also undertaken anew the investigation of the three products which form the title of this paper.

In order that the essential points of this discussion may be clearly understood, it may be stated in the beginning that attention has been specially directed to the consideration of the following observations or asser-

tions. As is probably well known, previous investigations have shown the oil of wintergreen to consist of methyl salicylate, associated with small amounts of a hydrocarbon or terpene, termed gaultherilene, and the oil of birch to consist of pure methyl salicylate. These statements the writer believes to be perfectly correct, and to present in a concise form the actual chemical composition of these oils.

Messrs. Trimble and Schroeter, in their recent paper (*loc. cit.*), affirm, however, that the oils of wintergreen and birch are both physically and chemically identical, that they both contain a hydrocarbon or sesquiterpene of the composition $C_{15}H_{24}$, which is present even to a larger extent in the oil of birch than in the oil of wintergreen, but that that from the oil of wintergreen has a lower melting-point. Furthermore that both of these oils contain small amounts of benzoic acid and ethyl alcohol, and that a representative sample of the artificial oil of wintergreen did not have the chemical composition of the natural oils, and was not pure methyl salicylate, but contained a large amount of methyl benzoate.

From previous observations, as well as from the results of the present investigation, I am forced to believe that most, if not all, of the foregoing conclusions of Messrs. Trimble and Schroeter are positively incorrect, so far at least as they relate to the pure oils in question; and this I hope to be able to demonstrate.

The oils examined by me in the present investigation were obtained from the following sources:—

I. *Natural Oil of Wintergreen*.—This was obtained directly from Mr. Robert B. Wilson, of Black River Falls, Wis., who had distilled the oil himself, and therefore no doubt could exist as to its absolute purity.

II. *Natural Oil of Birch*.—This was obtained from Mr. C. M. Driggs, of White Haven, Pa., the source from which Messrs. Trimble and Schroeter obtained their oil of birch, and at least one specimen of their oil of wintergreen.

Another small sample of the oil of birch in my possession represents a portion of the same oil as that used by Mr. Pettigrew in his investigation (*Amer. Journ. Pharm.*, 1883, p. 385).

III. *Artificial or Synthetic Oil of Wintergreen*.—This was kindly furnished me by Messrs. Fritzsche Bros. of New York, and was manufactured by their Leipzig House, Messrs. Schimmel and Co., who have made a specialty of this product.

PHYSICAL PROPERTIES OF THE OILS.

Specific Gravities.

These were determined in the present instance by means of a pycnometer, provided with an accurate and delicate thermometer, indicating tenths of a degree. All the specific gravities recorded represent a comparison of the oils with an equal weight of distilled water at the temperature of 15° C. The natural oils used for this determination had been once rectified, in order to remove traces of water and dark coloured oxidation products, such as are invariably formed when the oils are kept for some time. After this treatment they were perfectly clear and colourless.

I. *Natural Oil of Wintergreen*.—This was found to have a specific gravity of 1.1835 at 15° C., which is somewhat higher than that of a freshly distilled sample previously examined by me (*Pharm. Rundschau*, 1888, p. 209) namely 1.1766, or than that observed by Procter (*Amer. Journ. Pharm.*, 1842, p. 213 and 1843, p. 244), namely 1.173, but agrees well with that observed by Trimble and Schroeter (*Amer. Journ. Pharm.*, 1889, p. 399), namely 1.1838 and 1.1845.

II. *Natural Oil of Birch*.—The specimen of oil supplied to me by Mr. C. M. Driggs for this investigation, who assured me that it was perfectly pure, had the remarkably low specific gravity of 1.1606 at 15° C. The cause of this will be explained in connection with the chemical examination of the oil.

A new determination of the oil of birch used by Mr. Pettigrew gave a specific gravity of 1.1851 at 15° C. Trimble and Schroeter found the specific gravity of the oil of birch used by them to be 1.1840 at 15° C.

III. *Synthetic or Artificial Oil of Wintergreen.*—This was found to have a specific gravity of 1.1838 at 15° C. The product examined by Trimble and Schroeter is stated by them to be 1.1833 at 15° C.

Boiling Points.

These were determined in a glass fractionating vessel with a Geissler normal thermometer, so adjusted that the mercurial column should be entirely in the vapour of the boiling liquid. By this method the results admit of more accurate comparison, although the temperatures so recorded are probably 3 or 4 degrees higher than would be the case with a large portion of the tube of the thermometer exposed to the outer air. In each case the barometric pressure was also observed and recorded.

I. *Natural Oil of Wintergreen.*—This was found to distil quite constantly between 218 and 221° C., under a pressure of 731 millimetres.

II. *Natural Oil of Birch.*—The sample of this oil began to boil somewhat above 100° C., but the main portion of the oil distilled between 217 and 220° C., under a pressure of 734 millimetres. The cause of the low boiling-point of a portion of this oil, as well as its low specific gravity, previously alluded to, will be subsequently explained.

III. *Synthetic Oil of Wintergreen.*—This was found to boil very constantly at 221 to 223° C., under a pressure of 735 millimetres. Trimble and Schroeter record the boiling-point of the oils examined by them as follows: wintergreen 216° C., birch 217° C., and artificial oil of wintergreen 217° C. It would appear probable from this that they observed only the temperature at which the oils begin to boil, as it would be rare in the distillation of any amount of such a compound ether not to find the boiling point fluctuate within the limits of at least one or two degrees. If, moreover, the artificial oil of wintergreen examined by them contained such an amount of benzoic acid or benzoate of methyl as they have represented (about 15 per cent), it would seem strange that the boiling-point should not have been somewhat reduced, since benzoate of methyl is stated to boil at 198.5° C., under a pressure of 761 millimetres (See *Neues Handwörterbuch der Chemie*, Bd. I., p. 1084).

Optical Behaviour.

For these observations the Schmidt and Haensch improved form of the Soleil half-shadow polarising apparatus was employed. The degrees of rotation recorded by it would probably not agree with the angular rotation expressed by some other differently adjusted instruments, such as the polaristrobometer of Willd., although quite as useful in this instance for the purpose of comparison.

The natural oil of wintergreen obtained from Mr. Wilson, as also a sample of oil of wintergreen distilled in my own laboratory from fresh wintergreen leaves, deviates the ray of polarised light two degrees to the left, in a tube 200 millimetres in length.

The oil of birch obtained from Mr. Driggs, as also the specimen of oil of birch previously referred to as having been used in Mr. Pettigrew's investigation, and the artificial oil of wintergreen manufactured by Messrs. Schimmel and Co., have not the least action on polarised light. These observations serve to establish the following facts:—

1. That the oil of wintergreen supplied to me by Mr. Wilson was pure, since it presents the same optical and other physical characters as the oil distilled by myself.
2. That the natural oil of wintergreen contains a small amount of an optically active substance, which is not present in the natural and pure oil of birch.

This optical activity of pure wintergreen oil can of

course only be attributed to the small amount of terpene which it contains. The statement of Trimble and Schroeter that the oils of wintergreen and birch are physically identical, appears to be based simply upon the approximate agreement of their specific gravities and boiling-points.

That the pure oil of birch, which I maintain to consist simply of salicylate of methyl, as well as the synthetic oil of wintergreen, have no action on polarised light, is also quite in accordance with the numerous and well authenticated observations that all ordinary benzol derivatives in which the three double bonds of the C₆ nucleus remain intact, and which can consequently contain no asymmetrical carbon atoms, are optically inactive. (Compare Landolt, *Das optische Drehungsvermögen organischer Substanzen*, 1879, pp. 22 to 30 et seq.).

(To be continued).

THE POLLUTION OF STREAMS BY PAPER WORKS.

By JOHN C. THRESH, D.Sc., M.B.,
Medical Officer of Health.

IN the list of subjects submitted to Members of this Association as suitable for discussion before the Public Health Section was the one now introduced. I was led to select it because on several occasions I have had to examine the waste products from paper mills, to ascertain their effect upon the streams into which they were cast, and have also had to advise how the pollution of comparatively pure streams could be prevented, and to devise processes whereby the filthy river waters of Lancashire could be rendered sufficiently pure for use in the manufacture of paper.

A paper on such a subject as this must necessarily be more or less technical in character, but County Medical Officers and those aspiring to hold such positions will require to make themselves acquainted with many trade processes if they wish to become efficient in the discharge of their duties. In the short time allotted for the reading of the paper I will endeavour to give as clear an account as possible of the origin of the matters with which paper makers pollute our streams, and also of the methods which have been proved practicable for preventing such defilement.

The amount of polluting material produced by a paper mill depends upon its size, and also upon the kind of fibre-yielding material used, and the special quality or kind of paper manufactured. The largest amount is produced by the mills using Esparto grass for newspaper making, and the smallest by the makers of millboard and of brown and other coarse kinds of paper.

In order to realise the relative importance of the various waste products it will be necessary to enumerate the materials used in paper making, to classify the waste materials, and to briefly describe the processes by which they are produced.

The raw materials used in paper making may be grouped in three classes:—

1. The fibre-yielding materials. Esparto grass, straw, wood-pulp, rags, paper shavings, old sacks, ropes, cotton-waste, &c.
2. The chemicals used in preparing the fibre. Caustic soda (usually manufactured at the paper works from soda-ash and lime), chloride of lime, antichlor (sodium thiosulphate), &c.
3. The substances used in glazing, colouring, and weighting the paper. China clay, ultramarine, ochre, alum, glue, resin, &c.

The first stage in the process of paper making is the

* Read before the British Medical Association, Birmingham, 1890

beating or "dusting" of the raw material to remove as much as possible of the dirt and dust. The fibre-yielding material is then packed in large iron cylinders and heated under pressure with strong caustic ley. The usual charge of a boiler is 50 cwts. of Esparto or 20 cwts. of straw, with an amount of caustic ley corresponding to 17 or 18 lbs. of caustic soda per cwt. of material and about 1400 galls. of water. For rags a much smaller quantity of alkali is required, probably on an average only 3 lbs. of caustic soda to the cwt. Where prepared wood-pulp or paper shavings are used this boiling process is unnecessary, the material being already what is technically called "half stuff." After boiling the liquor is drawn off, and, in the majority of cases, is allowed to flow directly into the river. This waste ley, technically called "boilings," varies in composition with the nature of the material treated. The Esparto "boilings" are dark reddish brown in colour, almost black in bulk, and have a very characteristic balsamic odour. The reaction is strongly alkaline, and it froths very freely, even when largely diluted with water. It is the cause of the abundant froth found near the weirs on streams into which it is cast. I find the average density is 1060, and each gallon contains about 8000 grains of solid matter in solution, of which about 5000 grains consists of organic matter derived from the Esparto. Grass "boilings" are not quite so dark in colour, have no balsamic odour, and contain about 3600 grains of matter in solution, of which a little over 2000 are organic. The density is about 1030. Both contain a little caustic soda, the former, on an average, 500 grains, and the latter 100 grains per gallon of the "boilings." Rag boilings vary considerably in colour, strength, &c., according to the quality of rag treated. Most paper makers regard rag boilings as much more objectionable polluting agents than Esparto or grass boilings. When thrown into a stream with lime residues or waste bleach liquor a glutinous precipitate forms, adhering to the sides and bed of the river and, when exposed, readily decomposing and becoming offensive.

To make one ton of paper about two tons of Esparto or grass are required; the amount of organic matter therefore removed by the "boiling" and subsequent washing is simply enormous. On one small stream in Scotland I found there were six paper mills, casting into it every day 26 tons of solid matter, of which at least 12 tons was organic, and I know one large paper mill at Lancashire which alone throws daily into the adjoining stream fully this amount of polluting matter. At this mill no attempt was made to utilise any portion of these waste materials until I showed that one portion could be used for purifying the filthy river water in order to enable it to be used in the works. Unfortunately the sludge so produced is periodically flushed into the river, so that its last state is, if possible, worse than its first.

Returning now to the process of paper making. After the strong ley or "boilings" had been drained away, cold water is run into the boiler, and this, when drawn off, constitutes the "first coolings," and consists of ley about one-third the strength of the original "boiling." The washing process is repeated several times, producing second, third "coolings," &c., which of course consist of still further diluted ley. After the process of cooling is completed, the fibre passes to the "beating engine," to be pulped and washed with a still larger quantity of water. It is next transferred to the bleaching tanks to be treated with a clear solution of bleaching-powder, in the making of which another waste product arises—the calcium hydrate or insoluble portion of the bleaching-powder. During the bleaching process the hypochlorite of calcium in solution becomes converted into the chloride, and this solution is also thrown into the streams. After bleaching, the fibre is again washed, and finally with or without the addition of China clay, size, colouring-matter, &c., it passes on to the paper machine. The machine water, if containing the size, &c., is usually pumped back and used over and over again.

In making millboard and the coarser kinds of paper the bleaching and washing processes are considerably curtailed.

We are now in a position to classify and consider the various sources of river pollution from the paper making industry. We may divide them into two groups—the solids and the liquids.

The solids comprise—

1. The dirt and dust collected during the "dusting" of the fibre-producing material.
2. The carbonate of lime resulting from the manufacture of the caustic soda.
3. The insoluble portion of the bleaching-powder.

The liquids comprise—

1. The "boilings" and "coolings."
2. The washings from the pulping machine (breaking engine) and other waste wash waters.
3. The waste bleach.
4. The waste from paper machine containing size, colouring material, &c.

(We may take most of these seriatim).

The "dustings" are most considerable where Esparto is largely used. As it is rarely cast into the streams, and usually finds a ready sale for manurial purposes, we need not further consider it.

The lime residues are in most cases thrown, either openly or surreptitiously, into the rivers. There can be no excuse for such pollution. The lime residue from the soda-making process should be allowed to drain in tanks, made in duplicate. Whilst one is filling the other is draining, and, when sufficiently dry, should be carted away. In some districts the farmers would gladly avail themselves of it for agricultural purposes. The slacked lime forming the insoluble portion of the bleach should be utilised in causticising the soda ash.

Of the fluid polluting materials, by far the most important are the alkaline boilings and coolings, and these we will consider last. In the washings from the "breaker" engine the suspended fibrous material is the most objectionable constituent. These washings vary in composition during various stages of the process. A sample of mixed washings, when examined, contained in each gallon—

Matters in solution	52 grains.
Matters in suspension	170 "
Total	222 "

The reaction was faintly alkaline.

By passing this liquid through fine wire cloth "save-alls" a considerable portion of the fibre is recovered, but a portion passes through and remains in suspension. This strained fluid, especially if mixed with the waste from the paper machine containing size, &c., forms a turbid mixture which it is most difficult to treat. The solid particles settle very slowly, and rapidly choke up all kinds of filters. Where sewers are available, and provided the quantity is not too considerable, I see no objection to the strained solution being allowed to flow therein. As the washing processes are at present conducted an enormous amount of water is used, but it has been proved over and over again that if the fibre be more thoroughly washed by percolation before removal from the boilers the amount of water subsequently required for washing in the breaker engine is reduced very considerably. Such a change in the process of manufacture necessitates the use of a larger number of boilers in proportion to the paper made, and therefore the outlay of more capital, but on the other hand it is more economical because a much smaller amount of fibre is lost in the washing. Where no sewer is available, or the amount of turbid fluid produced is considerable, it may be passed through settling tanks and precipitation hastened by the addition of a little sulphate of alumina. The sludge

Source of sample.	P.c. of sewage.	P.c. of mill disch'ge.	Appearance.	Reaction.	Loss on Total solids.			Chlor- Nitrates. ides.	Nitrites.	Oxygen used.	Free Am.	Organic Am.
					Grains per gallon.	Parts per million.	Parts per million.					
1. Water from stream above all the mills.	—	—	Brown, peaty, turbid.	Neutral.	7'	3'	5	None.		1.8	0.12	0.50
2. Below two large paper mills.	0.2	5.6	Brown, with numerous flocculæ.	Do.	13'	5.5	1.0	Do.		5.2	0.10	1.10
3. Below all (6) the paper mills.	0.7	7.9	Do.	Faintly alkaline.	15'	6.0	2.4	Do.		7.6	0.11	1.80
4. Still lower, beyond a sewer outfall.	1.2*	7.6	Do.	Do.	31'	14.5	2.0	Large trace.		9.5	0.85	2.6

* Probably understated. Flow very variable

would have to be drained and carted away, possibly it would be used as manure. In most cases the effluent would be sufficiently pure to pass into the stream. Where a still higher standard of purity is for any reason required intermittent filtration through land as suggested by the Rivers Pollution Commissioners would have to be resorted to.

The waste bleach consists of a solution of calcium chloride with a little fibre in suspension. This might be mixed with the washings from the "breaker" engine and treated therewith, and the same may be said of the waste from the paper-making machine. Where the "boilings" are run into the river with the waste bleach is said to cause a flocculent precipitate settling in the deep pools and quiet corners. I do not regard this objection as well founded, especially in works where Esparto and straw are chiefly used, for I found on mixing fairly strong solutions the precipitate which formed settled very slowly, and became again diffused by the slightest agitation, and it showed no signs of adhering to the sides of the containing vessel. Dilute solutions (1 in 200) produced only a turbidity, and after standing 12 hours there was no sediment deposited. These experiments were conducted to ascertain whether the mixed liquors, if allowed to flow into a sewer, would tend to form a deposit therein. The conclusion I arrived at was that the alkaline fluid had a cleansing rather than a fouling action.

We must now consider the "boilings" and "coolings," which constitute by far the most serious source of pollution, both as regards quality and quantity. The objectionable constituents are the free alkali, the soap formed by the action of the alkali on the resinous constituents of the fibre, and the other organic matters also held in solution. In the first place the amount of these fluids should be reduced to a minimum by a more systematic and efficient method of removing the ley from the fibre. At the present time about two-thirds of the polluting matter is removed at each drawing off, so that the boilings, when withdrawn, leave one-third behind, the first coolings one-ninth, and the third one-twenty-seventh. By a little different manipulation three-fourths of the ley can be withdrawn each time, so that the "boilings" and "first coolings" together would contain fifteen-sixteenths, or nearly 94 per cent of the polluting matter. The next cooling would contain 4 per cent, leaving only about 2 per cent to be removed by further washing. The soda could then be recovered from the "boilings" and "first coolings," whilst the "second cooling" could be used for making fresh caustic ley. The further washings could be mingled with those from the breaker engine and treated therewith.

In a few mills the soda is recovered from the "boilings" only, the "coolings" passing into the river, and in a still smaller number of mills the "boilings" and first "coolings" are evaporated. The old method of soda recovery consists in evaporating the alkaline liquors in shallow open pans, to drive off the water, and partially

burn the residue. The solid matter is then fired in caves, for it contains a considerable amount of combustible matter, whereby the mass smoulders, leaving behind an impure soda ash. This process gives rise to a serious nuisance from the disagreeable odour evolved, and a very large amount of soda is lost in the dense fumes given off. Less than 50 per cent of soda is recovered by this primitive method.

The two more modern and most economical processes for soda recovery are the "Porion" and the "Yahyan." The "Porion" system is the invention of the late Émile Porion, a wealthy distiller of Wardrecques, Pas de Calais. A diagram of a section of the whole apparatus is exhibited. At the commencement of the apparatus are the fireplaces, behind this in succession are the calcining hearths, the combustion chamber, the "Porion" chamber, and the chimney. Over the calcining hearth and combustion chamber are placed shallow pans for heating the alkaline liquid by the waste heat. When this liquid has reached the boiling point it is allowed to flow into the "Porion" chamber, where it is dashed into spray and evaporated by the passage through it of the intensely heated air from the furnace to a suitable strength for further treatment. It is then run into a tank placed over calciners to keep it hot and fluid. It flows from here to the calcining hearth, where, by the action of the flame from the furnace, the organic matter is all consumed, and impure soda ash alone remains.

This process will recover 80 per cent of the soda ash at a cost of about £1 8s. per ton of 46 per cent ash.

The "Yahyan" system of evaporation was worked out by the American engineer whose name it bears. Here the evaporation is quite distinct from the calcination, and is effected in a "multiple effect" vacuum apparatus. (A diagram of the most recent form of the apparatus was exhibited). The liquid to be evaporated is passed through a series of tubes, each set of coils being enclosed in an iron cylinder containing superheated steam (25 lbs. pressure). By aid of a pumping engine and condenser, a high vacuum is maintained in the tubes in the last cylinder (four cylinders are employed in the most effective form of the apparatus). The fluid is passed continuously into the tube of the first cylinder, where it begins to boil vigorously, and is drawn rapidly forward, flowing out of the fourth cylinder in a condition suitable for introduction into any form of roaster or calciner. At the Esk Paper Mills, Messrs. Brown and Co. have adopted this process of evaporation, and calcine the residue in one of their patent Duplex Reversible Roasters. They state the cost of recovering the soda ash does not exceed 15s. per ton.

In the United States, where more attention is paid to the utilisation of by-products, still better results have been obtained. The recovery of soda from weak waste liquor has been brought to such perfection that not more than three to five cwt. of coal are used per ton of 48 per cent ash recovered, whilst the percentage of recovered ash, compared with the total consumption is from 80 to

90 per cent. These results are obtained by using the "Warren Rotary Furnace" and Yahyan evaporator. The waste heat from the furnace is utilised for raising steam to work the vacuum pump, so that the only coal used for the recovery of ash is that burned in the fire box of the rotary furnace. A large plant of this kind is now being erected at an English paper mill.

It is unnecessary for us to discuss the relative advantages and disadvantages of the rival systems. It is enough that we are satisfied that by either the paper manufacturer can not only get rid of his alkaline liquors, but do so at an actual profit to himself. A knowledge of the fact that this can be done, that the prohibition of the pollution of rivers by the alkaline leys will not prejudice the industry, is one of great importance to County Councils and all Sanitary Authorities having paper manufacturing within their districts. There needs be no anxiety about enforcing the law, and we may reasonably hope that before long some systematic attempt will be made in some country or district to compel all the paper makers to use the "best practical and available means" of treating their waste products, instead of casting them all into the rivers and streams, as is almost the universal practice now.

In conclusion, I append a table of analyses of the water taken from various points along the course of a river receiving the discharges of a number of paper mills, and the sewage from villages, &c., on its banks. The calculated percentages of sewage and fluid mill discharges are also given. Considering the large proportion of mill discharge, it will be noticed that the impurity is not so large as would be expected, but it must be remembered that these waste products are not passed in uniformly and continuously, but only at intervals, often during the night. In some cases also the lime residues are stored until the river is in flood, when they are boldly flushed in and rapidly carried away.

THE FIXATION OF ATMOSPHERIC NITROGEN.*

By A. A. BRENNEMAN, S. B.†

INTRODUCTION.

THE great industrial problem indicated in the title of this article has been before chemists for half a century. It is doubtful whether there has been any real progress towards its solution since the ending of the first attempts to manufacture cyanides commercially and economically made by Possoz and Boissiere, at Newcastle-upon-Tyne, in 1844-1847. It would seem that the development of chemical theory within the same period should have thrown some light upon the more obscure points of the process, and the author has attempted in the following pages to define the present aspect of the problem, theoretically as well as practically. That the treatment is inadequate to the greatness of the subject he is fully aware. The limitations of his own time have made a fuller inquiry impossible at present. He can only hope that others may be led to follow up the subject more thoroughly. There is room for further experiment in this direction, both in the laboratory and on a large scale. The fixation of atmospheric nitrogen is an industrial problem to be compared with that involved in the manufacture of ammonia soda or of water-gas, each of which passed through quite as discouraging an experience before attaining success as has, so far, been the lot of the nitrogen question. The question is still an open one, inviting further investigation. It has been taken up anew

in recent years by Berthelot, from the theoretical side, and by Weldon from the industrial or practical side, and there is nothing in theory or practice at present to warrant the assumption that it is a hopeless question; in commercial importance it outranks either of the processes mentioned.

The matter given herewith relates principally to the preparation of cyanogen. The question of the synthesis of ammonia has been put somewhat in the background for lack of time and space. It is evident, however, that the fixation of atmospheric nitrogen in any one form is the solution of the general problem.

PART I.—HISTORICAL SUMMARY.

SHOWING THE PROGRESS AND DEVELOPMENT OF PROCESSES FOR THE MANUFACTURE OF CYANOGEN AND ITS DERIVATIVES.

Prussian Blue.

The familiar colouring matter, prussian blue, was discovered about 1710, but the chemical substance cyanogen, the radical common to prussian blue and to a large series of complex substances now known to chemistry, was not isolated until more than a hundred years later. The name cyanogen (generator of blue) was given by Gay Lussac, in 1814, to the new substance which he found to be the characteristic ingredient of this blue and of compounds related to it. The familiar name of "Prussiates," still applied in trade to the double cyanides of iron and potassium, as well as the common name "Prussic Acid," by which hydrocyanic acid is known, bear evidence of the importance which the blue colour originating in Prussia had early acquired as a commercial product.

Some time before the year 1710* a German manufacturer named Diesbach, working with the so-called Dippel's animal oil (commonly obtained by destructive distillation of bones, blood, or other animal waste) happened, in handling a sample of this oil made from blood, to add to it a solution of potash (crude potassium carbonate) and obtained thereby a blue colour. The process was soon applied upon a commercial scale. It was first described in a book called *Miscellanea Berolinensia*, published in 1710. But the discoverer of the colour was not known by name until mentioned by Scheele in 1731.

Woodward and Brown, English chemists, each published a paper in 1724 upon the new blue. Woodward refers to a German from whom he had received directions for preparation of the blue, but gives no name.†

The process, as reported by Woodward, consisted in deflagrating a mixture of saltpetre and argols (crude potassium bitartrate) and fusing the product with dried blood. The resulting mass was lixiviated with water and the solution was treated with copperas and alum, producing a greenish precipitate, which on heating with hydrochloric acid, yielded the blue colour which has since been known as Prussian or Berlin blue. Brown (*loc. cit.*) substituted animal flesh for blood in the process. He also suggested that iron was essential to the colour of the new substance.

Geoffroy, in 1725, proposed the use of wool and charred horn instead of blood or flesh.

Scheele in 1731 published the name of Diesbach as the original discoverer. (R. W., *loc. cit.*)

In later modifications the use of nitre was abandoned and scrap iron was added to the mixture. The process as thus originated is, in its essential features, that which exists to-day for the manufacture of potassium ferrocyanide, from which prussian blue is made by precipitation with a ferric solution.

* "Richardson-Watt's Chemical Technology," vol. i., p. 1, *et seq.* (Referred to hereafter as R. W.)

† *Phil. Trans.*, 1724, 33-34, 15-25. In the original edition of the Transactions, Woodward's article is in Latin and the name of Diesbach is not mentioned. In the later, uniform edition the article is in English, and the name of Diesbach is given, in a foot note, as the German referred to.—B.

* *Journal of the American Chemical Society*, vol. xi., Nos. 1-2.

† The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

Potassium Ferrocyanide.

Macquer (1750—60?) first made ordinary yellow prussiate of potash (potassium ferrocyanide) in the crystalline form by treating prussian blue with a concentrated solution of caustic potash.

Beaumé in 1773 proved the presence of iron in the same salt. The fact that iron was an essential ingredient of the salt remained for a long time unknown; as the proportion of iron varied in blue from different sources it was regarded as an impurity and many attempts were made to prepare a blue free from iron. Berthollet (1800—1806) determined the iron quantitatively.

The researches of Gay Lussac, in 1814, first placed the composition of prussian blue and its related substances upon an intelligible basis by showing that they all contain the radical cyanogen, a compound of carbon and nitrogen (CN) which combines with hydrogen to form an acid and with metals to form simpler or complex cyanides, of which latter prussian blue, ferric ferrocyanide, $(Fe_7(CN)_{18})$ is a good example.

This knowledge at once led to inquiries into the chemistry of the commercial manufacture of yellow prussiate of potash, a process which had previously been purely empirical.

The researches of Liebig led to the general theory at present accepted, namely, that potassium cyanide is the first product of the fusion of nitrogenous animal matters with potash, and that the yellow prussiate found in the liquor after leaching the fused mass results from decomposition occurring between potassium cyanide and a compound of iron, generally ferrous sulphide, which is formed in the fused mass by action of metallic iron upon the sulphur of the animal matters. In proof of this view potassium cyanide can be extracted by alcohol from the fused mass previous to the addition of water.

Muspratt, in 1820 (*loc. cit.*) obtained by direct lixiviation of the fused mass crystallised yellow prussiate, which had been obtained previously, by the method of Macquer, from prussian blue.

Mackintosh in 1824 used closed pots for fusion and applied mechanical stirrers.

Gautier (*J. de Pharm.*, 1827, 11) suggested in 1827 and Gentile (*Dingl. pol. J.*, cxxix., 352) in 1835 practically applied the use of raw animal matter instead of charring it before fusion with potash, as had been done previously.

Naumann in 1837 allowed the flame to play directly upon the fused materials.

Up to this time the large loss of nitrogen during fusion and the small yield of ferrocyanide with respect to the theoretical yield (never more than one-third, generally much less) seems to have attracted comparatively little attention. But the increasing demand for the prussiates in dyeing, and the relatively greater cost of animal waste drew attention to the chemical problem involved in preventing this escape of nitrogen. It was found that the nitrogen was volatilised largely during fusion, as ammonia or organic bases, and the collection and utilisation of these was attempted.

Kuhlmann in 1838 (*J. pr. Ch.*, xxvi., 410) discovered that when ammonia was passed over red hot charcoal, cyanogen and ammonium cyanide were formed, and by using a mixture of charcoal and potash for absorption he obtained potassium cyanide.

The idea of obtaining cyanides by passing ammonia over hot carbon, however, was probably of earlier origin.

Jaquemyn, applying this idea, passed the vapours from the prussiate pots over hot charcoal to obtain cyanides, and Berry (*Eng. Pat.*, Jan. 21, 1840; *Jsb. chem. Tech.*, 1858, 184) patented the same principle.

These facts relating to the conversion of ammonia into cyanides by the action of hot carbon are of interest as showing the development of chemical ideas upon the subject of cyanogen. They had their origin, however, mainly in the practical experience of the prussiate manufacture, with its waste of nitrogenous vapours. Whatever interest they may have in connection with the history of

the subject, they probably would not have led to the idea of atmospheric nitrogen as a source of cyanogen, except for another discovery originating also in an industrial process.

Cyanogen from Atmospheric Nitrogen.

Zinken in 1813 (*J. pr. Ch.*, xxv., 246) had found a mass of fused salt mixed with carbonaceous matter in the lower part of a furnace at Rothebütte, which he partly examined and supposed to be principally chlorides. Koch (*loc. cit.*) found a similar mass at Königshütte in 1819. Berthier (*Jsb. chem. Tech.*, 1879, 28) also in 1826 remarked the presence of potassium carbonate as fused salt in the lower part of an iron furnace. No one seems to have tested these deposits or exudations for cyanogen until Daves in 1835 announced the existence of potassium cyanide in them. No quantitative determination was made.

In 1837 Neilson first introduced the use of the hot blast at the Clyde iron furnaces. Shortly afterwards,* a peculiar exudation of fused salt which hardened on reaching the air to a white, opaque mass was noticed upon the walls of the furnace near the boshes. The substance was regarded with much curiosity, and it is related by Clark, who made the first analysis of the product, that its alkaline character was soon discovered by the workman and that it was used by the wife of one of them, for a time, as a substitute for soap in washing clothes.†

Clark's analysis showed it to contain potassium cyanide 43·4 per cent, potassium carbonate 45·8 per cent. No ferrocyanide was present. The mixture gave no blue colour on addition of hydrochloric acid, but yielded a blue precipitate when ferrous sulphate (copperas) was added previous to the addition of the acid in excess. This furnace went on producing potassium cyanide for three years from this time.

Zinken and Bromeis (*J. pr. Ch.*, xxv., 246) found in the bottom of a hot blast charcoal furnace at Magdesprung in the Harz a carbonaceous mass containing iron and lead and a saline matter, which, on lixiviation, yielded the following potassium salts, namely, ferrocyanide, cyanide, carbonate, silicate, and manganate. A similar substance was noticed by Redtenbacher (*R. W.*, *loc. cit.*) in a hot blast furnace at Mariazell in Styria. Potassium cyanide was produced so abundantly in this case that it was sold commercially for galvanic gilding. The substance was found at the light hole, where the gases issue, and also in the pipes through which the gases pass from the furnace to the stove.‡

Bunsen and Playfair (*Report of British Association*, 1845) made an elaborate investigation of a furnace at Alfreton which yielded cyanides. The production of the substance was so abundant that it was estimated to amount to 224·7 lbs. in twenty-four hours. A hole was made in the front wall of the furnace, two feet nine inches above the tuyere or blast pipe, and the gases from that point were drawn off through a pipe for examination. Fumes of potassium cyanide escaped with the gases and condensed in the tube. Cyanides were obtained only from the lower part of the furnace; above the boshes none

* Probably produced more copiously in consequence of the action of the hot blast, as the circumstance had been only once reported before and has since been a common phenomenon of hot blast furnaces. Neilson had used the hot blast in iron furnaces as early as 1828, however. See "Bauer's Metallurgy of Iron," p. 175.—B.

† *Pogg. Ann.*, xl. 315; *Dingl. pol. J.*, lxxv., 466.
‡ I have, in my own experience, seen two cases of cyanide produced in blast furnaces. One from an anthracite furnace as an exudation from the wall below the boshes, the other from a furnace (at Irondale, West Va.), using coke, both, of course, hot blast furnaces. In the latter case no cyanides appeared upon the wall of the furnace, but a heavy, stony, grayish deposit formed in the downcast pipe through which the gases passed to the stove. It accumulated rapidly, forming a deposit like limestone in appearance, which threatened to clog the pipe and had to be broken away from time to time. Both samples were examined qualitatively, and found to be rich in cyanides. The gray colour of the second sample was probably due to coke dust. The mass was probably formed from spray or vapour of fused potassium cyanide, which, passing out of the furnace, condensed and solidified upon the wall of the pipe where it first became chilled, binding together, as it hardened, the furnace dust which accompanied it.—B.

were found. These chemists believe that cyanides were produced only at a temperature corresponding to that at which potassium oxide gives up its oxygen to carbon. In the higher parts of the furnace cyanogen acts as a reducing agent and is destroyed by oxygen from the ores. When cyanides fall as low as the tuyere, on the other hand, they are burned, according to these authorities, by the blast of air. The conditions necessary for their production, therefore, are a reducing (deoxidising) atmosphere or presence of hot carbon, and a temperature of the degree above mentioned.

Gases drawn from the furnace, as described above, had the following composition:—Nitrogen, 58.05 per cent; carbonic oxide, 37.43 per cent; hydrogen, 3.18 per cent; cyanogen, 1.34 per cent. These figures correspond to nitrogen 79.2 per cent, oxygen 22.8 per cent (instead of 20.08 per cent; oxygen corresponding to water found in the gases is deducted). There is evidently here a deficiency of nitrogen as compared with ordinary air. At two feet above the tuyere no oxygen nor carbonic acid was found in the gases.

R. F. Smith (*Ysb. chem. Tech.*, 1879, 44) in 1865 found a compound oozing from the crevices of an old blast furnace at Kilmarnock, which on analysis yielded 21.45 per cent potassium cyanate, 47.73 potassium cyanide, 10.13 per cent potassium carbonate.

A. v. Kerpely (*CHEM. NEWS*, 1865; *Ysb. chem. Tech.*, xi., 54) describes the escape of a quantity of fused salts, chlorides, and cyanides, from the slag hole of the blast furnace of Alsó Sajón in Hungary, just before the escape of the slag.

(To be continued).

NOTICES OF BOOKS.

The Maybrick Trial: A Toxicological Study. By C. MEYMOTT TIDY, M.B., F.C.S., and RAWDON MACNAMARA, F.R.C.S.I. London: Baillière, Tindall, & Cox.

INTENSE as was the sensation stirred up by the Maybrick trial, when the opponents of capital punishment, out of pure humanitarianism, threatened the Home Secretary with violence, the case presented little to excite the interest of chemists. It was not asked whether the right tests had been applied for the detection of the poison, whether there had been any neglect, oversight, or want of skill on the part of the experts employed for the prosecution. It is painful, we must add parenthetically, that experts are still retained for the prosecution or for the defence, instead of being employed by the court to explain the scientific phase of the question just as does the judge expound its legal aspects.

But this we let pass. No one denied that arsenic was discovered in the viscera, the flesh, &c., of James Maybrick. But the defence contended, and contends yet, that the quantity of arsenic found in the body, $\frac{1}{10}$ grain, or according to Prof. Stevenson $\frac{1}{10}$, was insufficient to cause death, or, at least, was very much smaller than the minimum quantity of arsenic which is recorded to have proved fatal. Further, it was shown that the deceased had been in the habit of dosing himself, and had, amongst other medicines, made use of arsenic.

Our authors further contrast the symptoms from which Mr. Maybrick actually suffered with those which ought to have appeared had he been under the influence of a fatal dose of arsenic. Supposing these two lists of symptoms to have been fairly enumerated and accurately described—a point on which our opinion is worthless—Dr. Tidy seems quite justified in saying that “everything, in short, it would seem, was present that ought to be absent, and was absent that ought to have been present, were it a case of arsenical poisoning,” and again, “the symptoms are not even consistent with arsenical poisoning.”

It will be observed that the authors lay more weight on

the evidence given by the witnesses for the prosecution at the coroner's inquest and the magistrate's inquiry than that actually produced at the trial. These remarks refer especially to the post mortem appearances. Dr. Humphreys before the coroner testified that there were patches of redness in the bowels, but made no mention of “petechiæ.” Two months later, at the trial, the same witness supplemented his statement by speaking of “a dotted condition of the stomach, the dots appearing like flea-bites.” Drs. Tidy and Macnamara here disclaim the inference which doubtless would be drawn in a certain quarter, viz., that “Dr. Humphreys had been looking up the subject of arsenical poisoning and possibly came across a drawing representing the usual condition of the stomach in such cases.” Here we are forcibly reminded of one of the defects of our system of obtaining the evidence of experts by examination and cross-examination. Such a witness may, we submit, easily forget some important fact, and if he afterwards wishes to correct his omission he is accused of inventing something to save his own credit and bolster up his case. Hence it would be much better if, instead of the catechetical method, scientific witnesses were required to give in a systematic written report, from which they could not depart.

Dr. Tidy is fully justified in insisting that the distribution of arsenic in the liver or in the intestines generally is anything but uniform. He quotes approvingly the late Dr. Letheby's advice: “Never examine a portion of the liver for a poison until you have mashed up the whole of it first.” Had Prof. Stevenson acted on this principle the sum total obtained might have been found less, or possibly much more than what he calculates.

If we remember rightly, in some cases where the ingestion of arsenic had been prolonged or was of old standing some of the poison was found to have accumulated in the brain—a part which, in this case, does not seem to have been submitted to analysis.

We may further ask whether it is prudent in toxicological inquiries to turn attention to the detection of one poison only, when possibly more than one may be present.

The “study” before us is drawn up with great ability, and confirms our impression that, whether as an expert witness or in his new capacity as a barrister, Dr. Tidy will prove a formidable antagonist.

CORRESPONDENCE.

GLASER'S ALCOHOL METHOD FOR IRON OXIDE AND ALUMINA DETERMINATION.

To the Editor of the Chemical News.

SIR,—A number of trials of the above method—which I have conducted in accordance with the directions given in *Zeitschrift für Angewandte Chemie*—have convinced me of its superiority as compared with the old processes involving the use of acetic acid. But it seems to be characterised by an imperfection that I should like to see removed if possible:—the liability, namely, of traces of the Fe and Al oxides to escape being collected on the filter. Whether from incomplete precipitation or from dissolving by the washing, a slight additional precipitate frequently shows itself in the filtrate and washings when boiled, and this necessitates re-filtering. I can never feel sure of having the whole of the iron oxide and alumina on the filter till after boiling the filtrate; and I sometimes find that traces of precipitate will appear even in the second filtrate when made alkaline and boiled.

I should be glad to know whether any of your readers have had similar experience, and whether they have been able to adopt any modification of the process that obviates the difficulty.—I am, &c.,

A.I.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 3, July 21, 1890.

New Researches on the Relative Stability of Salts, whether Alone or in Presence of Water. Salts of Aniline.—M. Berthelot.—This is in reality a thermo-chemical paper. The author takes the formation-heat of salts, referred to the solid state, as the measure of their relative stability. He compares the formation-heat of the properties of the aniline salts possessing a certain stability, such as the sulphate, nitrate, or chloride, with the unstable salts, like the acetate and the benzoate.

Formation-Heat of Certain Amides.—MM. Berthelot and Fogh.—The formation of the anilides from the solid and the gaseous base liberates more heat than that of the corresponding amides, a circumstance correlated with a greater stability as against the decomposing action of water. This stability results also from another cause acting in the same direction, the slight formation-heat of the aniline salts.

The Sensitiveness of Plants, viewed as Simple Reagents.—Georges Ville.—From the results given it appears that by means of beer-yeast it is possible to recognise the presence of 0.0005 grm. of phosphate in 1 litre of water, which corresponds to 5-10,000,000ths of the weight of the liquid. But agricultural plants are also reagents of an extreme delicacy and accuracy. The author gives as an example the sugar-cane, the dominant food of which is calcium phosphate. With the complete manure the cane gives a harvest of 57,000 kilos. per hectare. If we omit the phosphate the yield is only 15,000 kilos. Hence 600 kilos. superphosphate, containing 90 kilos. phosphoric acid, determine an excess of crop of 42,000 kilos. per hectare, which represents 70 times the weight of the phosphate and 466 times the weight of the phosphoric acid. If referred to the 4,000,000 kilos. of vegetable soil covering the surface of a hectare, the phosphate represents less than 1-6000th part of the weight of the soil and the phosphoric acid less than 1-40,000th. The author hopes to fix the limits of this method.

Researches on the Double Titanium, Tin, and Copper Phosphates.—L. Ouvrard.—Titanic acid dissolved in melted potassium phosphate yields two sorts of products. If relatively little titanic acid is employed, and if the mixture is slowly cooled, we obtain PO_5TiO_2 in cubo-octahedra, without action on polarised light. If the proportion of titanic acid is increased the result is a potassium phosphotitanate, $3\text{PO}_5\cdot 4\text{TiO}_2\cdot \text{KO}$, in small, nearly cubic crystals, strongly double-refractive. Stannic oxide furnishes products parallel to those of titanic acid. Copper oxide also, like the dioxides, yields double salts of the general formula $3\text{PO}_5\cdot 4\text{MO}_2\cdot \text{NaO}$, and $4\text{PO}_5\cdot 3\text{MO}_2\cdot 6\text{NaO}$.

Researches on Dispersion in Organic Compounds (Ether Oxides).—Ph. Barbier and L. Roux.—In examining oxides of formenic radicles the authors find that the dispersive powers B and the specific dispersive power $\frac{B}{d}$ increase with the molecular weight. Their values are almost the same for the different isomers of the same condensation in carbon. On passing from a compound to its superior homologue, the introduction of CH_2 into the mol. occasions an increase of molecular specific dispersive power = 8.2. The oxides belonging to the allyl radicle present an interesting peculiarity: in

place of varying with the molecular weight, B and $\frac{B}{d}$ have values approximately constant. The dispersive power augments as the proportion of hydrogen decreases. In the oxides containing the benzyl radicle the dispersive power diminishes as the molecular weight augments.

Certain Hydrates of Simple Ethers.—M. Villard.—The author undertakes to examine if ethers other than methyl chloride and bromide cannot furnish crystalline compounds with water. He has experimented upon methyl iodide, ethyl chloride, bromide and iodide, and methyl and ethyl fluorides. Of these bodies all except ethyl bromide and iodide have given the expected result.

On Oxygluconic Acid.—L. Boutroux.—Oxygluconic acid is not identical with glucuronic acid, notwithstanding the identity of their percentage composition:—(1) Glucuronic acid, on the evaporation of watery solution, furnishes an anhydride in large brilliant crystals fusible at 167° . Oxygluconic acid, if evaporated in the water-bath in like manner, yields merely a brown syrup which gradually blackens. (2) Glucuronic acid is dextro-rotatory; oxygluconic acid is lævo-rotatory. (3) Glucuronic acid is insoluble in alcohol, whilst oxygluconic acid is very soluble. (4) The potassium and sodium glucuronates, according to Herr Thierfelder, can be easily crystallised, whilst those of cadmium and calcium cannot. With oxygluconic acids the author has obtained the exactly opposite result. Yet oxygluconic acid approaches closely to glucuronic acid by its double function of a monobasic acid and an aldehyd.

Detection of Impurities contained in Alcohol.—Ed. Mohler.—The sulphuric acid reaction cannot serve to determine the impurities in alcohol, and it can merely serve to detect the presence of products which are colourable by sulphuric acid. Rosaniline disulphite gives an approximate idea of the quantity of aldehyd contained in a commercial alcohol if we compare it with a standard solution. Aniline acetate in an acid solution is the special reagent for furfural. Upon other solutions of aldehyds, alcohols, and ethers its action is negative. It may serve for the colorimetric determination of furfural. Potassium permanganate is reduced by pure ethyl-alcohol as well as by the impurities in question, the only difference being in the time required.

A New Process for Determining the Mineral Matter in Sugars by Means of Benzoic Acid.—E. Boyer.—(See p. 64).

The Mineral Springs of Cranson.—Ad. Carnot.—The nature of this paper is sufficiently shown by its title.

Combinations of Hæmoglobine with Oxygen.—Christian Bohr.—In company with the well-known compound oxyhæmoglobine there exist at least three others, all of which are dissociable, and have the same spectrum, but do not contain the same proportion of oxygen. There exist four oxyhæmoglobines containing respectively per grm. about 0.4 c.c., 0.8 c.c., 1.7 c.c., and 2.7 c.c. of dissociable oxygen. Hæmoglobine may combine at once with oxygen and carbon dioxide.

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THE CHEMICAL NEWS.

Vol. LXII. No. 1603.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

FROM the singular result obtained with sulphur chloride on poppy oil and mixtures containing this oil, I was inclined to believe that this oil was peculiar in yielding a black or very dark pasty magma; I therefore prepared a little from the seeds of the Horn poppy (*Glaucium flavum*), and from the seeds of the *Papaver somniferum*, by expression and by percolation with solvents.

As poppy oil is said to be largely used for adulterating olive oil, I thought it would be interesting to find out whether the source of adulteration was from an unknown plant, or whether the behaviour was due to changes brought about by time. Poppy oils recently made yielded light coloured products; those which had been a little time in hand yielded darker products; whereas those which had been obtained a long time ago gave black pasty magma. Similar products were obtained from mixtures containing these oils; hence the oxidation process was suggested for bringing about in a few hours what some months' ordinary exposure would require.

I give here the results obtained on poppy oils, 5 grms. being used in each case:—

No. of sample.	Sulphur chloride.		Iodine abs. per cent. Original oil.	Remarks.
	Magma.	Soluble.		
1.	6.46	1.958	131.1	Four yrs. old.
27.	6.36	1.538	135.0	
74.	6.08	2.382	92.4	Very old.
29.	6.50	0.692	135.2	Gl. fl. express.
50.	6.55	0.629	139.1	
86.	6.46	0.768	140.7	Gl. fl. by CS ₂ .

The iodine absorption shows the variation arising from oxidation. The weight of magma by sulphur chloride shows that the yield of soluble matter is increased as the total weight is reduced. Sample 74 gave a black pasty magma. Oils extracted by solvents yield less than those obtained by expression. Oils thickened by oxidation (blown oils) give less total magma than the same oils not blown.

The following results were obtained with rape oil and cotton oil:—

No of sample.	Sulphur chloride.		Iodine abs. per cent. Original oil.	Remarks.
	Magma.	Soluble.		
7.	6.03	0.606	58.4	Thickened rape.
40.	6.41	0.178	112.9	German rape.
38.	—	—	101.8	English rape.
42.	6.13	0.351	104.9	Colza.
41.	6.19	0.318	98.9	"
47.	5.87	0.833	71.6	Thickened cotton.
57.	6.18	1.514	127.5	Refined "
22.	6.22	1.397	118.7	"
21.	6.28	1.300	112.4	Crude "

The conclusion is that the thickened oils yield less magma than the same oils not thickened or oxidised. The product from the former is darker in proportion to the extent of oxidation, and from the consequent loss of glycerin the soluble extract is greater. In addition to these remarks, cotton oil not thickened gives a very large proportion of soluble matter, and this is probably not due entirely to changes introduced by refining, for the crude oil product also yields a large proportion of soluble matter

to CS₂. Experiments with sulphur chloride on sample 47, as regards the soluble matter, show that oxidation has rendered some of the oil insoluble.

As a general rule, the drying oils give the greatest yield of total magma, and which is for the same oil nearly proportional to the iodine absorption. Oils extracted by solvents give a smaller yield of magma and have a lower iodine absorption than the same oils drawn by pressure. The results obtained on linseed oil and walnut oil (30) from the decorticated nuts were as follows:—

No. of sample.	Sulphur chloride.		Iodine abs. per cent. Original oil.	Remarks.
	Magma.	Soluble.		
3.	6.36	0.844	162.4	By CS ₂ .
46.	6.34	0.936	162.6	"
44.	6.45	0.724	170.1	Pressure, hot.
45.	6.57	0.603	176.3	" cold.
81.	—	—	172.7	"
30.	6.55	0.536	150.6	Walnut, by CS ₂ .

Oils drawn by hot pressure have a low iodine absorption; this is due to the liability of such oils to oxidise in manufacture.

Boiled linseed oil gives a dark pasty magma, similar to old poppy oil; this might have been expected, if we bear in mind that the object in boiling is to obtain an oxidised oil which assists in drying.

CHEMICAL COMPOSITION OF THE OILS OF WINTERGREEN AND BIRCH, AND THE CHARACTERS OF THE SYNTHETIC OIL OF WINTERGREEN.

By Prof. Dr. FREDERICK B. POWER,
University of Wisconsin.

(Continued from p. 68).

Chemical Examination of the Oils.

I. Natural Oil of Wintergreen.—400 grms. of this oil were decomposed by heating on a water-bath for about two hours, in a flask provided with a reflux condenser, with a solution of 200 grms. of caustic potassa. The liquid was then further diluted with water, and distilled until oil drops ceased to come over. This distillate was then again separately distilled, in order to bring the drops of oil, or the terpene, within a smaller compass, and thus more easily effect its separation from the water. The liquid or terpene so obtained had precisely the same properties as that isolated by me on a former occasion, and was also in this instance only contained in the original oil to the extent of a small fraction of one per cent. It is a somewhat viscid, yellowish liquid, possessing to a marked degree the pepper-like odour described by Cahours, and has a specific gravity of about 0.940, as recorded in my former paper.*

The hydrocarbon separated by Messrs. Trimble and Schroeter from the oil of wintergreen, as also from the oil of birch, by extracting the saponified oil with ether or petroleum ether, they state to have the following remarkable properties. "The products both solidified on standing for a day or two, or at once on cooling. That from wintergreen commenced to melt at 10° C., and was clear at 15° C., but the hydrocarbon from birch did not commence to melt below 18° C. and was clear at a few degrees above that temperature," &c.

In connection with this statement I may say that the terpene obtained by me from oil of wintergreen, in the manner above described, does not separate any solid matter when kept for three hours in a freezing mixture at a temperature of 10° C., but remains perfectly transparent. It is difficult to believe that a pure terpene, as separated

* Pharm. Rundschau, 1888, p. 209

from a volatile oil, would solidify at any such temperature as that above noted.

Notwithstanding the probability that the substance experimented with by Trimble and Schroeter was a mixture, from their vapour density determination of it they assign to it the molecular formula $C_{15}H_{24}$. In the latter determination they appear to have employed the method of Victor Meyer, as they state that a certain amount of the substance displaced a certain amount of air. Why they should have taken the pains to record these figures, without at the same time giving the other physical constants which enter into the calculation of the molecular formula, it is difficult to conceive; for such an isolated statement does not permit of a re-calculation of their results, and can therefore of itself possess no scientific value.

In order to confirm, if possible, the correctness of this statement, I have also attempted to obtain the vapour density of the liquid separated by me from the wintergreen oil. It was first deprived as much as possible of any adhering moisture by allowing it to remain for some time in contact with freshly ignited potassium carbonate, and the method of Victor Meyer was then employed,* with the use of a paraffin-bath. In the first determination the temperature of the bath was somewhat above $300^{\circ}C$, and in the second the temperature was somewhat above the boiling point of mercury, but in both instances the liquid under examination was observed to vaporise very slowly, and at the same time to become completely decomposed, with the separation of a tarry substance. Concordant results could therefore not be obtained, nor could they under such circumstances be regarded as possessing any scientific value.

In my former paper† the results of such a determination, as recorded in the *Neues Handwörterbuch der Chemie*, Band III., p. 343, were noted, where the boiling point of this terpene is stated to be $160^{\circ}C$, and its vapour density 4.74, which agrees with the molecular formula $C_{10}H_{16}$. Although having had previously no occasion to doubt the accuracy of this statement, it would now not seem possible that it could be correct as applied to the substance separated by me on different occasions from true wintergreen oil, for its viscous character would indicate a much higher boiling point, and it certainly cannot be vaporised without considerable decomposition. That it may belong to the class of polyterpenes is possible, and the application of Raoult's method‡ for the determination of its molecular weight might be attended with success, but the very small amount of substance available has prevented my further examination of it in this direction.

The original, strongly alkaline liquid remaining in the flask after the distillation of the terpene was subsequently shaken with ether, but the latter, on evaporation, afforded simply a small amount of a dark coloured resinous substance. From the alkaline liquid the salicylic acid was then separated by means of pure hydrochloric acid, and, after being collected on a strainer, and washed, was recrystallised from boiling water. The further examination of this acid will be subsequently referred to.

II. *Natural Oil of Birch.*—This oil, as previously stated, was obtained from Mr. C. M. Driggs, of White Haven, Pa., who had supplied Messrs. Trimble and Schroeter with the oil examined by them, and who had assured me of its perfect purity. Its low specific gravity, 1.1606 at $15^{\circ}C$, led me, however, in the beginning to believe that it possessed a somewhat abnormal chemical composition, although it was considered that this might indeed be due to the fact that it contained a considerable amount of a terpene, especially since Trimble and Schroeter have stated this oil to contain more of the latter than the oil of wintergreen. It will be remembered,

on the other hand, that the original oil had no action on polarised light.

Three hundred grms. of the oil in question were treated in a manner similar to that described in connection with the oil of wintergreen. After the process of saponification had been completed, a considerable amount of a light liquid was observed on the surface of the alkaline mixture, which was separated as completely as possible by means of a pipette, and placed in contact with freshly ignited potassium carbonate. The strongly alkaline liquid in the flask was then further diluted with water, and distilled, in order to recover the remaining portion of the hydrocarbon. On finally shaking the alkaline mixture contained in the distilling vessel with ether, and allowing the latter to evaporate, only a small amount of dark coloured, resinous matter was obtained, as in the case of the pure oil of wintergreen.

The liquid separated in the above manner from the oil of birch amounted to 13.5 grms., or 4.5 per cent of the original oil. The amount actually present, with consideration of a little unavoidable loss, was therefore probably about 5 per cent. Its specific gravity was 0.8066 at $15^{\circ}C$, and upon distillation it was found to possess no constant boiling point. It commenced to boil somewhat above $100^{\circ}C$, and about one-fourth of the liquid distilled over below $220^{\circ}C$, about one-half between the temperatures of 220° and $270^{\circ}C$, and the remainder, which was allowed to remain in the distilling flask, was dark coloured and somewhat viscid. The portion of liquid distilling below $270^{\circ}C$ was perfectly colourless, and, as would naturally have been inferred by the behaviour of the original oil, was without any action on polarised light. It was then subjected to analysis, with the following result:—

I. 0.1115 gm. of substance gave 0.1365 gm. H_2O = 0.0152 gm. H, or 13.63 per cent H; and 0.3290 gm. CO_2 = 0.0897 gm. C., or 80.45 per cent C.

After once redistilling over sodium, it was again analysed.

II. 0.1815 gm. of substance gave 0.2205 gm. H_2O = 0.0205 gm. H, or 13.49 per cent H; and 0.5420 gm. CO_2 = 0.1477 gm. C., or 81.37 per cent C.

	I.	II.
C.. ..	80.45 per cent.	81.37 per cent.
H	13.63 "	13.49 "
	94.08	94.86

It was evident from these results that the liquid in question was a mixture of hydrocarbons, containing some oxygenated bodies, which I did not attempt to completely remove, as its character had already become sufficiently revealed.

That it was a mixture, and not a simple body, was clearly shown by the inconstancy of its boiling point, and the latter, as well as its optical inactivity and low specific gravity, also proved quite conclusively that it was not a terpene. It was furthermore found not to be acted upon by powdered iodine, nor by strong nitric acid or sulphuric acid, and possessed, especially when allowed to evaporate on the hand, the unmistakable odour of petroleum. All the characters of the substance, both chemical and physical, have indeed conclusively established the fact that it is simply kerosene oil. That the gentleman who supplied me with this sample of the oil of birch believed it to be perfectly pure, I have not the slightest doubt, as it was not distilled by himself, but an enquiry as to how such a contamination could occur has elicited neither any explanation nor a reply. In any event it is not probable that the opinion would be advanced that petroleum is a natural constituent of the oil of birch, even though birch trees may grow in close proximity to the oil wells of Pennsylvania.

The chemists of Messrs. Schimmel and Co., Leipzig, have found this adulterant in both cassia oil and citron-

* *Berichte der Deutsch. Chem. Ges.*, 1878, II., p. 2253.

† *Pharm. Rundschau*, 1888, p. 209.

‡ *Comptes Rendus*, Tome 64, p. 1517; 95, p. 188; 96, p. 1653; as also *Pharm. Zeitung*, 1889, p. 617.

ella oil,* but I believe the use of petroleum for the adulteration of oil of birch has not hitherto been observed. In consideration, however, of this fact, it would seem not unreasonable to suppose that the solid substance separated from the liquid obtained by Trimble and Schroeter from oil of birch might have consisted of a paraffin, rather than a terpene, for, as I have shown, the terpene separated from a pure oil of wintergreen does not possess any such properties as they describe. They also mention the fact that by the distillation of the saponified oil of birch they obtained but 0.084 per cent of the so-called terpene, whereas by extracting the alkaline mixture with petroleum ether 0.447 per cent was obtained. If the substance in question were really a terpene, at least such as those at present known to occur in volatile oils, it should not have been impossible to have recovered it by distillation with water.

The results of this investigation may also serve to throw some light upon the following remark of Dr. Squibb, in his paper on "The Oil of Wintergreen as a Therapeutic Agent" (*Ephemeris*, vol. iii., 1887, p. 953), "Oil of birch is said by Pettigrew to be pure methyl salicylate, but this can hardly be true of the oil accessible in the markets, since several authorities state that in distilling the oil the distillation begins many degrees below the permanent boiling point." In the writer's opinion there is now no reason to doubt but that the oil of birch hitherto found in commerce, having the characters thus referred to, was not a pure natural product, but, like the specimen examined by me, was contaminated to a greater or less extent with petroleum.

The examination of the oil of birch by Mr. Pettigrew† was conducted under my observation in the Chemical Laboratory of the Philadelphia College of Pharmacy, and, although several years have since passed, I can distinctly remember that after the saponification of the oil, and subsequent distillation with water, no trace of oil drops could be observed in the distillate, so that if any terpene or other hydrocarbon were present it could not have amounted to more than very insignificant traces.

The small sample of oil of birch now in my possession, which represents a portion of that examined by Mr. Pettigrew, is not sufficient to admit of confirming his results by the method of saponification and subsequent distillation. I have already shown, however, that this oil possesses a quite constant boiling point (219–221° C.), and that it is completely devoid of action on polarised light. I have also recently subjected it to ultimate analysis, with the following result:—

0.2460 grm. of substance gave 0.1180 grm. H_2O
= 0.0131 grm. H, or 5.32 per cent H; and 0.5665 grm.
 CO_2 = 0.1545 grm. C, or 62.80 per cent C.

Calculated for methylsalicylate:—

	$C_9H_8O_3$	Found.
C	63.16 per cent	62.80 per cent
H	5.26 "	5.32 "
O	31.58 "	31.88 "
	100.00	100.00

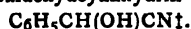
A pure methyl salicylate could hardly afford more closely agreeing analytical numbers, and I must therefore maintain my former opinion, in confirmation of that expressed by Mr. Pettigrew, that the natural oil of birch consists of pure methyl salicylate, and is not perfectly identical, either chemically or physically, with the natural oil of wintergreen. Competent observers, such as Dr. Squibb and Professor Maisch, are, moreover, capable of recognising a distinction in the odour of the two oils.‡

Messrs. Trimble and Schroeter have endeavoured to support their argument that the oil of birch does not

consist of simple methyl salicylate by the statement (*loc. cit.*, p. 398) that "it is the exception when a product as simple as oil of birch is described by Pettigrew to be is produced in nature, such substances are more frequently found to be made up of a series of compounds."

It is very evident from this expression that the authors have either forgotten or are unaware of the fact that oil of birch is regarded as belonging to the class of so-called ferment oils,* and that it is the rule, not the exception, that such oils are quite simple bodies, or at least are not made up of a series of compounds. As a prominent example of this class it is only necessary to mention the volatile oil of mustard, consisting of the sulphocyanate of allyl, C_3H_5-NCS , and although this oil in its pure and natural condition may sometimes contain small amounts of carbon bisulphide, the presence of the latter has been quite satisfactorily proved to be due to a secondary reaction of the acid potassium sulphate formed in the fermentative process on the mustard oil itself.†

As another example of an oil of simple composition of this class, which is familiar to most chemists, may be mentioned the oil of bitter almonds, consisting of benzaldehyde, C_6H_5-COH , with small amounts of hydrocyanic acid. Even the relatively small amount of the latter present in this oil can not be set forth as an argument in favour of its complex character, for, in the light of recent investigations, the product of the reaction of emulsin on amygdalin in the presence of water is a simple chemical compound, which has received the appellation of benzaldehydcyanhydrin—



After the separation of the petroleum from the oil of birch, as previously described, the alkaline mixture was treated with pure hydrochloric acid, and the salicylic acid thus obtained, together with that from the oil of wintergreen, will be subsequently referred to.

(To be continued).

COLORIMETRIC METHOD FOR ESTIMATING THE MORPHINE STRENGTH OF LAUDANUM AND OTHER PREPARATIONS OF OPIUM.

By S. J. HINSDALE, Fayetteville, N.C.

PREPARE an official tincture of opium with assayed opium. You will know the morphine strength of this tincture.

Make three dilutions of it with dilute alcohol, as follows:—

One 3 parts tincture and 1 part dilute alcohol.
One 2 " " " " " "
One 1 " " " " " "

Put 12 c.c. of the tincture and of the dilutions in vials, and add to each 12 c.c. dilute alcohol—cork well and keep them as standard dilutions of known strength. Label them Nos. 1, 2, 3, and 4. Let the dilute official tincture be No. 1. Dissolve 0.04 gramme potassic ferridcyanide in 500 c.c. water and add to it fifteen drops *Liquor Ferri Chloridi*. Call this *Ferridcyanide Mixture*. (This must be freshly prepared, as it will be partly decomposed in a few hours). Prepare it in a glass stoppered bottle with water entirely free of iron.

Place four 50-c.c. clean glass tumblers or wine-glasses on a white surface and deliver with a pipette (about one-third filled) one drop of the dilutions in the glasses, commencing with No. 4 (the weakest), blowing out the

* See Schimmel and Co.'s *Bericht*, April, 1889, pp. 10 and 20; also *Pharm. Rundschau*, 1889, pp. 122 and 269-270.

† *Amer. Journ. Pharm.*, 1883, p. 385.

‡ *Ibid.*, 1885, p. 586, and *Ephemeris*, vol. iii., 1887, p. 953.

* See Procter in *Amer. Journ. Pharm.*, 1843, vol. xv., p. 246.

† *Pharm. Zeitung*, 1887, p. 543; and *Pharm. Rundschau*, 1887, p. 266.

‡ *Pharm. Zeitung*, 1887, p. 694; *Pharm. Journal*, 1887, p. 537; and *Proc. Amer. Pharm. Assoc.*, 1888, p. 484.

pipette after each dropping. (The pipette should be about four inches long, and made of $\frac{1}{4}$ -inch tubing, and should deliver drops of the dilutions weighing about 0.016 gramme or $\frac{1}{2}$ grain. To test the pipette, see how many drops will balance a 0.200-gramme weight. The reason for using so small a drop, and for diluting the tincture, is because a full drop of the undiluted tincture would develop too deep a blue colour).

Now add to each glass about 5 c.c. ferridcyanide mixture (it is convenient to use a homœopathic vial as a measure), and in about one minute add 15 or 20 c.c. water, and observe the shades of colour. This observation must be made *within five minutes*, as the air and light will soon cause all to be uniformly blue.

By comparison with the shades of colour produced by these standard dilutions, you can easily estimate the strength of any sample of laudanum with much accuracy. The sample must, of course, be diluted with an *equal part of dilute alcohol*. The presence of tannin interferes with this method, but opium does not contain tannin. Tannin is easily detected with a solution of a salt of iron. The ferridcyanide mixture *must be freshly prepared* and the glasses must be *clean and clear*, as the slightest bluish tinge interferes. Wash them with caustic soda and then with hydrochloric acid and rinse if they are soiled with Turnbull's blue.

The ferridcyanide mixture is probably the best confirmatory test for morphine. If one drop of water containing 0.00001 gramme of morphine is mixed on a white slab with one drop of the ferridcyanide mixture a blue colour will be developed within *one minute*. With water alone the mixture will become of a bluish shade in about *ten minutes*, owing to the action of air and light.

To estimate the strength of vinous or aqueous compounds of opium, they must be brought to about the same specific gravity as the "standard dilutions" with alcohol, that the drops may be uniform in size.

THE DRY ASSAY OF TIN ORES.*

PART I.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Continued from p. 59).

IV. The Assay in Detail.

THE different methods of assaying black tin in the dry way may be grouped under two heads:—

a. Those which aim at finding the actual amount of tin contained in the ore.

b. Those which determine approximately how much metallic tin can be recovered by treatment on a large scale.

The first class divides, according to the character of the resulting metal, into methods (a) yielding a button of metallic tin, and those (b) yielding an alloy of tin with copper or iron.

Class A (a).

1. *The German Method of Assay.*—This method, as given by Kert† and by Balling‡, is as follows:—

Five grms. of ore are intimately mixed with 0.75 to 1 gm. of charcoal dust, and charged into a clay crucible; on top are placed 12.5 to 15 grms. of black flux (or the substitute, two parts of potassium sodium carbonate and one part of flour), with 1 to 1.25 grms. of borax glass, then a salt cover, and finally a piece of charcoal. The crucible is covered, heated in a muffle or a pot-furnace at a moderate, gradually increasing temperature until the boiling has ceased, and then for from half to three-

quarters of an hour at a white heat. The crucible is removed from the fire, broken when cool, and the tin button weighed.

The process that takes place is simple. With the gradually rising temperature the tin becomes reduced to the metallic state by the charcoal, with which it has been intimately mixed, while any ferric oxide contained in the cassiterite will be reduced only to ferrous oxide and taken up by the slag. At a certain stage the black flux, or the flour of the substitute, becomes decomposed, the result being that finely divided carbon is uniformly distributed through the flux. This hinders any particles of stannic oxide from combining with the alkali when fusion begins, and assists the reduction of particles of ore that have not been completely converted into metal by the charcoal. The active fluxes—potash, soda, borax—combine with the gangue contained in the ore and form a slag; the neutral salt cover assists in making the slag liquid, and thus favours the collecting of tin particles, and prevents prills from adhering to the sides of the crucible; the charcoal finally, being slowly consumed, furnishes the reducing atmosphere above the charge. When the reactions have taken place and the fusion has become tranquil, the different parts settle according to their specific gravities: at the bottom, the tin button; next, the borax slag; above this the salt slag; any unconsumed charcoal remaining on top.

In carrying out the assays the above method was closely followed. The crucibles were size F, of the Battersea make; the charcoal was made to pass a 40-mesh sieve before it was mixed with the ore; the black flux substitute—two parts of potassium carbonate and one part of flour, to which 1 gm. of borax glass had been added—was used for flux.

The charge melted readily, and the slag was very thin, showing when cool a smooth surface. The crucible was not corroded by the fluxes, and no particles of tin were visible at the sides. On breaking it the salt slag separated readily from the borax slag, the former being coarsely crystalline and brittle. It had a resinous lustre, was subtranslucent, and of a dark purple colour. This colour must be attributed to finely divided carbon resulting from the charcoal on top. On dissolving the slag in water, a fine black slime remained. This proved to be pure carbon, and the solution showed only a trace of iron. The borax slag was vitreous, hard, subtranslucent, and olive-green. The button separated well from the slag, was white, bright, easily cut, and malleable; scrapings were not attracted by the magnet, showing the absence of iron. The tin, however, did not all collect in the button, as usually happens with tin assays. Prills remained suspended in the slag, and some adhered to that part of the crucible in contact with it. In the assays the salt slag, the borax slag, and the lower part of the crucible were ground together and screened through a 40-mesh sieve. The scales of each set of assays were weighed together, and the fine pulp of the same set panned, and the resulting fine tin weighed. It seemed advisable to do it in this manner, because the amount of scales and siftings in the separate assays was so small that it might easily have caused an error in the results.

If the percentage of tin recovered in the assays Nos. 1, 2, 3, 67.58 per cent, and in Nos. 4, 5, 6, 67.46 per cent, be compared with the actual amount of tin present, 67.84 per cent, it will be seen that the results obtained by this method are all that could be desired. The two averages differ only by 0.12 per cent, which is also very favourable. That assays Nos. 1, 2, 3 agree accurately is mere accident. It will be seen that 67.40 per cent collected in the button, and that only 0.28 per cent was scattered through the slags and adhered to the crucible. Assays Nos. 4, 5, 6 agree within 0.2 per cent. Less tin was collected in the button than in Nos. 1, 2, 3, and the total result is slightly lower, although still very good, *i.e.*, accurate within 0.5 per cent.

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 2.

† "Metallurgische Probirkunst," Leipzig, 1882, p. 412.

‡ "Die Probirkunde," Brunswick, 1879, p. 391.

* Berthier, "Traité des Essais," 1847, vol. ii., p. 473.

TABLE II.
Resulting Tin.

No. of Assay.	Total.		In button.		In scales.		In siftings.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
1.	3'379	67'58	3'37	67'40	—	—	—	—
2.	3'379	67'58	3'37	67'40	—	—	—	—
3.	3'379	67'58	3'37	67'40	—	—	—	—
Average..	3'379	67'58	3'37	67'40	0'001	0'02	0'008	0'16
4.	3'380	67'60	3'31	66'20	—	—	—	—
5.	3'370	67'40	3'30	66'00	—	—	—	—
6.	3'370	67'40	3'30	66'00	—	—	—	—
Average..	3'373	67'46	3'303	66'06	0'015	0'30	0'055	1'10

To see what influence would be produced by variations of time and temperature, assays Nos. 7 to 10 were made, increasing the time to two hours with Nos. 7, 8, 9, 10, and keeping Nos. 9 and 10 hotter than Nos. 7 and 8, and these last hotter than Nos. 1 to 6.

(To be continued).

RECOVERY OF ABSORBED MORPHINE FROM THE URINE, THE BLOOD, AND THE TISSUES.*

By THEODORE G. WORMLEY, M.D., LL.D.,
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University of Pennsylvania.

(Continued from p. 67).

Recovery of Morphine by Amyl Alcohol.

In the following examinations in regard to the application of amyl alcohol for the extraction and recovery of morphine, Kahlbaum's alcohol was employed. It was apparently perfectly pure, and had a density, as observed by a picnometer, of 0'811, at 20° C.

Amyl alcohol is about wholly insoluble in water, but a limited quantity of water is dissolved or taken up by the alcohol. If 100 volumes of the alcohol be agitated with 20 volumes of water, after complete separation of the liquids, the alcoholic liquid will measure 109 volumes, the aqueous being reduced to 11 volumes. In other words, under these conditions one volume of water is taken up by 11'11 volumes of the alcohol, with a corresponding increase of volume of the latter liquid.

On digesting excess of finely powdered pure morphine with amyl alcohol at the ordinary temperature for some hours, with frequent agitation, one part of morphine is taken up or dissolved by about 150 parts by weight of the alcohol. Under the action of heat one part of morphine may be dissolved in about 50 parts of the hot liquid. A hot saturated solution of this kind, after cooling and standing one hour, will still contain one part morphine in about 62 parts of the alcohol; after standing twenty hours, one part in about 82 parts of the alcohol. The salts of morphine are more or less extracted from their aqueous solution by amyl alcohol, differing in this respect somewhat according to the form of salt present. On dissolving, in the form of a salt, the equivalent of 25 m.grms. pure morphine in 5 c.c. water, agitating this solution with 25 c.c. pure hot amyl alcohol, then allowing the mixture to stand for twenty hours, the clear amyl alcohol held in solution, of the morphine, as follows:—

	Amyl alcohol extracted. M.grms.	Aqueous solution retained. M.grms.
Morphine, as acetate ..	8'93	16'07
" " sulphate ..	4'2	20'8
" " hydrochloride ..	3'6	21'4

* From the University Medical Magazine

Under similar conditions, only that 25 c.c. of amyl alcohol already saturated with water were employed, the following results were obtained:—

	Amyl alcohol extracted. M.grms.	Aqueous solution retained. M.grms.
Morphine, as acetate ..	5'0	20'0
" " sulphate ..	2'8	22'2
" " hydrochloride ..	2'5	22'5

These results indicate that on extracting an aqueous solution of a salt of morphine with pure amyl alcohol, a very notable portion of the alkaloid may be taken up by the alcohol; that this proportion may be diminished by first saturating the alcohol with water, and, finally, that a greater proportion of the alkaloid is taken up when in the form of acetate than when present either as sulphate or hydrochloride.

In the extraction of morphine in its free or uncombined state from the urine, by amyl alcohol, the results are more or less interfered with by the large proportion of urea taken up by the alcohol.

On digesting excess of finely powdered urea with hot amyl alcohol, and allowing the mixture to stand some hours, it was found that the liquid still held in solution one part of urea in 78'8 parts of the alcohol.

A still more serious interference is the extraction by the alcohol of certain extractive matters of the urine, which, having a strong reducing action, may mislead in regard to some of the tests for morphine.

Cases Examined.

CASE I.—A dog, weighing 10 kilos., whose bladder had just been emptied by means of a catheter, was given, Nov. 7th, 1889, 3'0 grms. (46 grains) of pure morphine, dissolved by the aid of acetic acid in 10 c.c. water, the solution being introduced into the stomach by means of a tube.

Within ten minutes the animal became very drowsy; soon thereafter there was great stupor, but a slight noise would startle the animal. After about one hour there was great weakness or partial paralysis of the hind legs. At the end of twenty-four hours the animal was much better, the weakness of the hind legs having disappeared; but it remained more or less drowsy for fifty hours, when it was killed by being bled to death.

1. Urine.—A.—Obtained from the animal by catheterisation, two hours and forty minutes after administration of the morphine, 12 c.c. turbid urine. This was acidulated with hydrochloric acid, and then extracted by agitation with two volumes hot amyl alcohol, which had already been saturated with water. After decanting the alcohol, the aqueous fluid was rendered alkaline by ammonia, and again extracted by two volumes hot amyl alcohol, and finally washed with a fresh portion of the alcohol. The alcohol thus employed was passed through a filter previously moistened with amyl alcohol and evaporated to dryness.

The alcoholic residue was treated with a little acidulated water, the solution filtered, then rendered alkaline by ammonia, and again extracted by hot amyl alcohol. The residue from the evaporation of this alcohol was treated with a little water, a drop of acetic acid added, the liquid filtered, then concentrated to a small volume. Slight excess of ammonia was now added, and the liquid allowed to evaporate spontaneously.

On applying to this residue the principal tests for morphine, they promptly indicated the presence of a very notable quantity of the alkaloid. After washing out the crystallised urea present with a little cold water, the morphine was obtained partly in the crystalline state. The total quantity of morphine present in the residue was estimated at about four m.grms.

B.—Withdrawn by catheter twenty-two hours after administration of the morphine, 160 c.c. urine, having a strong alkaline reaction, and which strongly effervesced on addition of hydrochloric acid, due to the presence of ammonium carbonate. Evaporated the urine to 60 c.c., cooled, and strained. Extracted the strained liquid, while still acid, with about two volumes hot amyl alcohol, previously saturated with water.

The aqueous liquid, after decanting the alcohol, was treated with slight excess of ammonia and extracted by two volumes hot amyl alcohol. This was decanted, filtered, and evaporated to dryness.

Minute portions of the residue thus obtained clearly indicated, by Froehde's reagent and other tests, the presence of morphine in considerable quantity.

The residue was treated with a small quantity of acidulated water, the solution filtered, then rendered alkaline, and again extracted by hot amyl alcohol. The residue from the evaporation of this alcohol was extracted in like manner a third time by amyl alcohol.

The final residue was treated with about 5 c.c. water acidulated with acetic acid, and the filtered solution treated with slight excess of ammonia. Very quickly crystals of morphine separated, and there was finally obtained from the solution, after washing with cold water and with ether, 24 m.grms. of finely crystallised, nearly colourless morphine.

It may here be noted that on washing the urea from a residue consisting of morphine, urea, and extractive matters, with cold water, the morphine will be dissolved greatly in excess over its solubility in pure water. This excess may sometimes be recovered, in part at least, by concentrating the liquid to a small volume, adding a trace of ammonia, and allowing the mixture to stand in a closed tube for some days or longer; the morphine may then separate in the form of colourless crystals, even from highly coloured liquids.

2. The Blood.—Fifty hours after the administration of the morphine, the dog still being strongly under the influence of the drug, 300 c.c. of blood was obtained from the animal. This was treated with 500 c.c. strong ordinary ethyl alcohol, 5 c.c. of acetic acid added, and the whole frequently agitated in a strong cylinder during two days. Decanted the liquid, and pulverised the solids in a mortar, returned the mass to the liquid diluted with water to 1000 c.c. and moderately heated the mixture. The cooled liquid was strained and the solids washed and preserved for future examination (**B**).

A.—The strained liquid was concentrated, filtered, and finally reduced to 50 c.c. It was then rendered alkaline by ammonia, and extracted with twice its volume of pure hot amyl alcohol. This was separated, filtered, and evaporated to dryness; and the residue thus obtained, after solution and filtration, was again extracted by fresh hot amyl alcohol.

The residue from the second amyl alcohol extract, when treated in the usual manner, furnished 14 m.grms. morphine, chiefly in the crystalline state, but rather highly coloured.

B.—In order to ascertain whether the above albuminous solids still contained a notable quantity of morphine,

which might be recovered by a stronger acid, the mass was treated with 500 c.c. water and 10 c.c. hydrochloric acid, and allowed to stand one day. The mixture was then largely diluted with water and again allowed to stand.

As the mixture was slimy and would not strain, it was about neutralised by sodium hydroxide, then strongly acidulated with acetic acid. The liquid was then strained, concentrated, filtered, and finally reduced to 100 c.c.

This, after addition of ammonia, was extracted with hot amyl alcohol; and the residue obtained on evaporating this liquid extracted a second time by a fresh portion of amyl alcohol.

From the second alcoholic extract, 8.5 m.grms. of very nearly pure morphine were obtained.

3. Liver.—The liver was cut into small shreds, these crushed in a mortar, and extracted at a moderate heat with 500 c.c. water strongly acidulated with acetic acid.

The solution thus obtained was filtered, then reduced to 100 c.c., rendered alkaline, and extracted with twice its volume of hot amyl alcohol. The residue from this alcohol was extracted a second time, and this in turn a third time, with fresh portions of amyl alcohol.

From the final alcoholic extract, 41 m.grms. of essentially pure morphine were obtained.

4. Brain.—The brain was removed immediately after the death of the animal. It presented a rather anæmic condition, being free from any signs of congestion.

The organ was crushed in a mortar, and extracted with diluted alcohol strongly acidulated with hydrochloric acid. The final aqueous solution obtained was extracted by amyl alcohol, and the purification by the alcohol repeated a second and third time.

The final residue clearly showed the presence of morphine, but the total quantity present was very minute.

5. Stomach.—An examination of the contents and scrapings of the stomach, consisting of little else than glairy mucus, showed the presence of morphine in very minute quantity. So far as known, the animal did not vomit, nor did it take any food after the administration of the morphine.

CASE II.—Injected hypodermically into the side of a dog, weight about 10 kilos, 1.0 gm. pure morphine, dissolved by acetic acid in 10 c.c. water, the bladder of the animal having previously been emptied by means of a catheter. The animal soon showed the ordinary symptoms of the poison, but after some days fully recovered. The urine was withdrawn and examined as follows:—

a. Two hours after administration of the morphine, 20 c.c. urine of feeble acid reaction was obtained. This was directly neutralised by ammonia, and extracted by hot amyl alcohol. This liquid, after filtration and evaporation, left a residue which readily showed the presence of morphine in decided quantity. After a second extraction by amyl alcohol, and further purification, 19 m.grms. of nearly colourless crystals of morphine were obtained.

b. Five hours and a half after, the injection obtained 40 c.c. of slightly alkaline urine. This was reduced to 20 c.c., and then extracted by amyl alcohol. The residue from this extraction, when purified as before, furnished 23.8 m.grms. crystallised morphine.

c. Twenty six hours after, the injection obtained 80 c.c. urine of slightly acid reaction and sp. gr. 1.016. This, rendered alkaline by ammonia, was extracted directly by amyl alcohol. The residue obtained from this extract, when further purified, readily showed, under several tests, the presence of morphine, but repeated efforts failed to obtain it in the crystalline state.

d. Twenty-eight hours after, the injection obtained 20 c.c. urine. From this obtained very satisfactory evidence of the presence of morphine, but only in the amorphous state. The quantity present was obviously much less than in the preceding examination.

e. Seventy-two hours after, the injection obtained 60

c.c. of urine. This still clearly showed the presence of morphine, but in further diminished quantity.

f. Twenty c.c. urine obtained at the end of ninety-six hours still showed under Froehde's reagent the presence of morphine, but beyond this reaction the results were doubtful.

CASE III.—Injected subcutaneously 0.2 grm. morphine, in 10 c.c. water, into a dog. This was the same animal used in last experiment, but twelve days thereafter. Marked symptoms appeared within ten minutes.

a. Two hours after the injection obtained 28 c.c. urine. This was concentrated to 14 c.c., and extracted in the usual manner. The final residue readily showed the presence of morphine, but the alkaloid was not obtained in the crystalline state. Fine crystals of the chromate, however, under the action of potassium chromate, were obtained.

b. Five hours and a half after the injection obtained 50 c.c. urine of acid reaction and sp. gr. 1.016. This was concentrated to 20 c.c., and extracted in the usual manner. The final residue showed the presence of morphine in perhaps somewhat larger quantity than found in the previous examination, but it was obtained only amorphous.

c. From 14 c.c. urine withdrawn at the end of twenty-eight hours the final residue, after purification by ether, gave under Froehde's reagent very marked morphine reactions.

(To be continued).

THE FIXATION OF ATMOSPHERIC NITROGEN.*

By A. A. BRENNEMAN, S.B.†

(Continued from p. 73).

THE facts just given had an important influence upon chemical thought. The source of the large quantities of nitrogen combined in the cyanides thus obtained became a subject of active discussion. It was not at once admitted that the free nitrogen of the air could be taken into combination with carbon to form cyanogen under the conditions existing in the blast furnace. The tendency was, at first, rather to find the source of nitrogen in the fuel or in the ammonia of the air. But the answer was given in a series of accurate experiments which left no room for doubt, and the direct fixation of atmospheric nitrogen by hot carbon under given conditions has long been accepted as a fact in chemistry.‡

The paper of Bunsen and Playfair was read before the British Association in 1845, but to take up the discussion methodically we must go back a few years. As has been said, the production of cyanides in the blast furnace at once raised the question of the source of the combined nitrogen, and the problem suggested by the furnace was soon transferred to the chemical laboratory.

Lewis Thomson, of Newcastle-upon-Tyne, in 1839 (*Dingl. pol. J.*, 73, 281) first proved that potassium cyanide is produced when coke, potash, and iron filings are heated to a high red heat in contact with air, and he received the medal of the Society of Arts for his discovery. Priority is claimed for Defosses, who made a similar discovery about the same time at Besancon in France.

Fownes and Young (*J. pr. Ch.*, xxvi., 407) also con-

firmed these statements in 1841, using carbon prepared from cane sugar and pure potash.

Erdmann and Marchand, however, in 1842 (*J. pr. Ch.*, xxvi., 412) repeated Fownes's experiments and reported that the process was uncertain and required very exact regulation of conditions to produce any cyanides at all. They concluded that no cyanogen is produced when the materials are perfectly dry.

Berzelius (*J. b. d. fortschr. d. Chem.*, 1844, 23) remarked that these results of E. and M. agreed with the earlier results of Wöhler, in that water was shown to be necessary to the reaction. It was suggested that water plays the part of an intermediary in the reaction, first forming ammonia, which is then converted into cyanide.

Langlois (*Ann. ch. phys.*, [3] i., 117) discussed the question raised by Erdmann and Marchand. He made two experiments. 1. Moist, purified air was passed over a mixture of pure carbon and potash heated to high redness. Cyanogen was obtained. 2. Dry air under the same conditions also yielded cyanogen. The production of cyanogen in each case was tested by converting it into prussian blue in the solution obtained from the fused mass of carbon and potash. He found, however, that if a lead glazed earthen tube were used instead of a porcelain tube, no cyanogen was obtained—lead in the glaze apparently decomposing cyanogen—and he ascribes the errors of Erdmann and Marchand to this fact.

Bunsen and Playfair (*B. A. Rep.*, 1845) also attacked this question in their investigation above quoted. They passed nitrogen over a mixture of pure carbon and potash heated to high redness in a tube and obtained potassium cyanide. As the nitrogen was free from ammonia and the materials were chemically pure the origin of the nitrogen in the cyanide was placed beyond doubt.

Rieken (*Dingl. pol. J.*, cxxi., 286) by very careful experiments confirmed the conclusion of Bunsen and Playfair as to the formation of cyanogen from pure carbon and nitrogen at a high temperature. He obtained pure carbon by heating pure cane sugar, and pure potash by igniting pure crystallised potassium bicarbonate. The mixture of carbon and potash was then put into a tube and heated to whiteness, and nitrogen, prepared from air, was passed over it. This nitrogen was prepared by passing air through strong sulphuric acid and then through calcium chloride—thus removing both ammonia and water—then over iron filings heated white hot in a gun-barrel and finally through the mixture of white hot potash and charcoal. The highest white heat was required and the previous heating of the nitrogen was found to be essential. When the temperature was below whiteness no trace of potassium cyanide was formed.

Delbrück (*J. b. Chem.*, i., 473) added further to the weight of evidence in favour of the conclusion of Bunsen and Playfair. He showed that the direct union of carbon and nitrogen was incontestable and extended the limits of existing knowledge upon the subject by describing other related reactions in which cyanogen is formed. Nitric oxide and "potassium carbonic oxide" were shown to produce cyanogen when heated. Carbon dioxide (CO₂) mixed with ammonia, or even with nitrogen, when passed over hot metallic potassium, or ammonium carbonate kept in contact with fused potassium, also yielded cyanogen.

The fact of the direct union of nitrogen and carbon being settled, and the practicability of carrying out the reaction on a commercial scale having been, in a certain sense, proven by the accidental phenomena of the blast furnace, attempts were made to build up a new manufacture, in which cyanides should be made direct from the nitrogen of the air.

The first patent taken out in England for manufacture of cyanides on the new principle was by A. V. Newton. (*Dingl. pol. J.*, xcvi., 293; Eng. Pat. No. 9985, Dec. 13, 1843) A patent taken out in 1839 by John Swindells (Eng. Pat., No. 8036) for the manufacture of cyanide

* *Journal of the American Chemical Society*, vol. xi., Nos. 1-2.

† The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

‡ The experiments of Bunsen and Playfair showed also that, on the small scale and with a very slow current of nitrogen, all of the nitrogen was absorbed by the hot mixture of potash and carbon. It is much to be regretted that no record of the composition of the escaping gases was made in the commercial manufacture of cyanides by Possoz and Boissiere.—B.

• The compound of the potassium retort (?)—B.

might have come partly under the same head, as it involved the fusion of potassium or sodium sulphate, coal and iron in a reverberatory furnace. A portion of the nitrogen of the fire gases might have been taken into combination under these conditions as an alkaline carbonate is formed, but the process avowedly looked only to fixing the nitrogen of the coal as cyanide.

The specification of Newton especially prescribes that nitrogen from any source, but free from "oxidating substances," be forced through a layer of small pieces of charcoal saturated with "pot-ashes" and heated to redness, the vapours containing cyanides to be absorbed by suitable liquids. He states that oxygen decomposes the cyanides at high temperatures; the necessity of excluding oxygen has always been recognised by other writers upon the subject as an essential feature of the process.

Newton used either charcoal, coal, or coke, but preferred the former, in pieces the size of a hazel-nut. The charcoal was saturated with a strong solution of potash and dried before being put into the retort. A definite maximum proportion of alkali was used; an excess prevents complete absorption of nitrogen and a deficiency involves loss (of carbon?). Twenty-five to one hundred parts of potash are used to one hundred of coal, according to the density of the latter. Nitrogen should always be in excess, but must not be passed too rapidly. A certain pressure upon the gas and much friction with the solids through which it passes are favouring conditions.

Newton recommends the use of waste gases from the sulphuric acid chambers after passing through ferrous sulphate and lime-water, to remove oxides of nitrogen. The use of these chamber gases has also been suggested by Binks, Firman, and others ("R. W.," vol. i., Pt. 5, 61-65).

Before the date of Newton's patent, however, Possoz and Boissiere (*Jsb. chem. Tech.*, 1855, 83; 1858, 191; *Dingl. pol. J.*, civ., 446; cvii., 444; cxix., 361; cxlix., 56) had been at work upon the same industrial problem in France, and had in operation at Grenelle, near Paris, in 1843, a small plant which was turning out yellow prussiate at the rate of 15,000 kilos., or more than fifteen tons per annum. The high price of fuel and the need of a cheap and abundant supply of highly refractory clay for making the retorts used in the process led them to remove, in 1844, to Newcastle-upon-Tyne, England, where they went into the operation on a large scale, under the patronage and co-operation of Bramwell and Hughes. The works here, in 1845, turned out yellow prussiate at the rate of more than a ton a day. They were run until 1847, and were then abandoned after considerable loss. The salt was said to be produced at the rate of less than two francs per kilo., and was of exceptionally fine quality.

This is the most persistent attempt on record to establish commercially a process for the fixation of atmospheric nitrogen, and as such deserves close consideration.

The process consisted of passing the gas from a coal fire through large vertical cylinders or retorts of fire clay filled with a mixture of wood charcoal and potash. The charcoal was prepared by saturating it with a solution of potash and then drying. Much stress was laid by P. and B. upon exclusion of water in the process. The retorts were kept at the highest possible temperature—a white heat being preferred—as the rate of conversion of potash into cyanide was found to be proportional to temperature. The conversion was commonly completed after ten hours, but 2-3 hours in some cases was sufficient, with a good white heat. The cyanised charcoal was withdrawn at the bottom of the cylinder and dropped into a tank of water containing powdered spathic iron ore in suspension, by which the cyanides were converted into ferrocyanides or prussiates. The solution was finally filtered and evaporated to crystallisation. The apparatus worked continuously.

In the French experiments the retorts were seven to eight feet long with walls 2-3 inches thick. In England, much larger and heavier retorts were used. The high temperature, in connection with the alkalies, caused rapid destruction to the retorts. They were heated white hot before the introduction of the alkalis. White hot flues also served to superheat the nitrogen or furnace gases before entering the retorts. In later forms of the apparatus air was admitted directly to the cylinders, oxygen being removed in passing through the upper layers of carbon. The presence of carbonic oxide or carbon dioxide, as in the fire gases, was found to be disadvantageous. Coke yielded less cyanogen than charcoal. The production of cyanide was said to be greater for a given weight of potash than by the old prussiate process. The alkalis charcoal contained 30 per cent of potash. Soda was found inferior to potash and required a higher temperature. Water, even in small quantities, hindered the production of cyanogen. This fact was ascribed by P. and B. to decomposition of the latter by water to form ammonia.

In the latest constructions the cylinders were 10 feet in length and 2 feet in diameter with walls 9 inches in thickness. These were built of fire brick, and their massive character enabled them to retain heat and to resist wear so as to last several months in use. Lateral slits were also made in the walls of the cylinders for admission of air direct, and through these slits the contents could be stirred to prevent clogging by fused potash, which had been one of the chief obstacles in the process. The current of gas was upward and the charcoal was fed in at the top in moist condition and dried thus by waste heat. A pump drew the gases through the cylinders.

The causes of failure assigned in England were the rapid destruction of apparatus owing to corrosion of the retorts by the alkali, and the great loss of alkali by volatilisation, or absorption by the cylinders. Much potash was wasted in the fine charcoal after lixiviation or converted into silicates and other salts useless for further application in the process. Bramwell (*Dingl. pol. J.*, civ., 446) patented some of the later improvements of P. and B.'s plant which were devised by him (Eng. Pat., Oct. 8, 1846). He preferred to convert oxygen of the air into carbonic acid rather than carbonic oxide before carrying it into the cylinders. The use of lateral slits is also a feature of his patents.

This process is said also to have been applied at several places in France, but was ultimately abandoned.

R. Laming, in 1843 (Eng. Pat., No. 9832, July 13, 1843), patented a process for manufacture of hydrocyanic acid by passing ammonia through red-hot charcoal.

Swindell, in 1844 (Eng. Pat., June 12, 1844), patented a process in which nitrogen or air or oxides of nitrogen were passed through charcoal or other carbonaceous material, heated to full redness in a perfectly close retort. If ammonia is to be formed, steam is mixed with the nitrogenous gas.

J. Laming obtained a patent in 1845 (Eng. Pat., No. 10,955, Nov. 18, 1845), (for another party), by which charcoal or other form of carbon in powder is mixed with alkali and the mixture is kept in fusion while a current of ammonia is passed through it for the production of cyanides.

Bunsen (*Rep. Brit. Assoc.*, 1845) proposed the construction of a furnace for the production of cyanides on the plan of the blast furnace. It was to be charged with alternate layers of coal and alkali and the fused cyanide was to be drawn off periodically at the bottom (*ante*). No industrial application of this idea is known, although Binks is said (R. W., p. 66), to have taken out a patent for a similar furnace.

Armengaud patented in France, in 1846, a furnace for manufacture of cyanides from the nitrogen of the air. (*Dingl. pol. J.*, cxx., 111 (with diagram); *Genie Industriel*, 1853, 315) Unlike P. and B. he regards the presence of steam as favourable to the process and prescribes its

* A cut of P. & B.'s furnace is given in "R. W.," p. 63.

its regular admission to the furnace. The charcoal, which must be in excess, is intimately mixed with potash, soda, or lime, the mass is heated to a cherry red, and over it is passed a mixture of furnace gases and steam. The absorption chamber resembles a reverberatory furnace. The product is leached with water at 75–85° C. The volatile products from the furnace are carried into a solution of ferrous sulphate.

F. Ertel in 1846 took out a French patent for a process very similar in principle to the above (*Dingl. pol. J.*, cxx., 77; French Pat., Nov. 16, 1846) involving the use of steam, or better, as the inventor says, of hydrogen. Air from a coal fire is passed through a column of coal or coke heated to a cherry red, and from this through a mixture of charcoal powder and alkaline carbonates or lime, also heated to cherry red. The distinctive features of Armengaud's and Ertel's process are the use of steam and the application of a comparatively low temperature, whereas Possoz and Boissiere insisted upon a white heat and the exclusion of steam as essential conditions.

The history of later attempts to utilise the nitrogen of the air for the manufacture of cyanides, shows, up to the present time, no commercial success. The few further plans or suggestions bearing upon the question are added here as having a possible bearing upon the future study of it.

Marguerite and Sourdeval in 1862 (*Jsb. chem. Tech.*, 1873, 361; *Ber.*, 1873, 79) found that when air is passed over a hot mixture of baryta and carbon, nitrogen is absorbed freely, forming barium cyanide, and that this compound in presence of steam at 300° C. yields ammonia. In another form of the process they passed a mixture of illuminating gas and nitrogen over a mixture of coal and barium carbonate. The resulting barium cyanide was decomposed in solution by potassium sulphate. They also used iron filings in one of their methods similar in other respects to the foregoing. This process, which seemed to promise much for the industrial uses of nitrogen, has never received any commercial application, even as a source of ammonia. (*Comptes Rend.*, l., 1100; *Dingl. pol. J.*, clvii., 73, 357) English patents for the process were taken out by Clark.

Diess in 1873 (*E. Meyer, Jsb. chem. Tech.*, 1874, 442) patented in France a method for the manufacture of cyanides which differs in no essential feature from that of Possoz and Boissiere (*ante*).

S. Q. and A. Brin, in 1883 (*Eng. Pat. No. 5802*, Dec. 18, 1883), patented a process for manufacture of ammonia by passing moist nitrogen over coke containing baryta, which recalls that of M. and S. They also utilised oxygen separated from the air by another process.

Berthelot (*Jsb. chem. Tech.*, 1869, 260; *Comptes Rend.*, lxvii., 1141; *J. pr. Ch.*, cvii., 272), in 1868, made a valuable contribution to the theory of the synthesis of cyanogen. He obtains acetylene (C_2H_2) by direct combination of its elements (under the influence of the electric spark) and converts this in presence of nitrogen by the same means into hydrocyanic acid (HCN). He says that when nitrogen acts upon a highly heated mixture of nitrogen and potash, the compound potassium acetylene (C_2K_2) is first formed, and that this, by direct union with nitrogen, forms two molecules of potassium cyanide (KCN).

J. Blair (*Scientific American*, 1878, 21, with cut, *Dingl. pol. J.*, ccxxx., 93) in 1878, patented an apparatus in the United States for manufacture of cyanides. Gases from a coal fire (a stack with a deep layer of coal) are drawn over a layer of heated iron ore to form carbonic acid by oxidation of the carbonic oxide. The former is absorbed by passing the gases through milk of lime, and the resulting nitrogen is carried to a holder. The nitrogen is then carried upwards through a hot mixture of potash and charcoal in a stack heated externally by a fire in a larger stack which encloses it. The charcoal is drawn from the bottom and leached. Fumes of potassium cyanide which escape from the stack are condensed in a chamber adjoining

ing and the lighter fumes are absorbed by a solution of a salt of iron.

Walter Weldon, in 1879 (*Jsb. chem. Tech.*, 1879, 472), obtained a patent in England for the manufacture of cyanides. He finds that the temperature necessary for absorption of nitrogen by alkaline charcoal is not so high as has been supposed.* Instead of a white heat, Weldon finds that a comparatively low temperature, a bright red, or even a lower heat, suffices to produce cyanides from mixtures of alkalis or alkaline earths with carbon in presence of air. His apparatus consists of a rotatory furnace similar to that used in preparation of black ash (soda ash).

V. Alder, in 1881 (*Jsb. chem. Tech.*, 1881, D. R. Pat. 12,351; 1882, 509), brought forward a method involving some new features. Oxides, hydrates, or carbonates of the alkalis or alkaline earths with charcoal are used to absorb nitrogen prepared by passing air or fire gases through solutions of potassium, or barium sulphide, or by passing air over iron, copper, or zinc. He asserts that presence of finely divided metallic iron is useful in the process,† and supplies this by saturating charcoal or coke with a solution of ferrous sulphate and then igniting it in a current of hydrogen. Sulphates and sulphides of the alkalis are also used, together with lime, in place of other alkaline bodies above mentioned. In a later patent (D. R. Pat., No. 18,945, 1881), the admixture of hydrocarbon gases or carbonic oxide with the nitrogen is recommended; also the fuel in fragments is coated with a pasty mass made by mixing a strong solution of a soluble salt with charcoal powder, sawdust, &c. These modifications are introduced with the object of increasing the surface available for absorption of nitrogen.

Ludwig Mond, in 1882 (U. S. Pat. 269,302, Dec. 19, 1882), obtained a patent for manufacture of cyanides and ammonia by calcining, out of contact with air, a mixture of carbon, barium carbonate, or oxide, and magnesia, previously compressed into blocks, and then exposing these heated blocks to a current of nitrogen. In an improvement he first heats the nitrogenous gas by passing it through hot barium salts, and then passes it through fresh layers of barium salts and carbon at the temperature required for forming cyanogen compounds.

Fogarty (U. S. Pat. 288,323 and 402,324, Nov. 13, 1883), in 1883, took out two patents in the United States for production of cyanides and ammonia, which consisted essentially in dropping a mixture of powdered carbon and alkali into superheated furnace gases or superheated "generator gas" (a mixture of nitrogen, hydrogen, carbon monoxide, and steam), whereby cyanides were produced, which were subsequently decomposed by steam, yielding ammonia. He also obtained two similar patents in 1887 (U. S. Pat. 371,186, and 371,187, Oct. 11, 1887). In one of these processes the mixture of superheated furnace gases or generator gas is mixed with steam in excess, with the object, as explained by the author, of first producing cyanides and cyanates, and then, in the same mixture, decomposing these by the steam present to produce ammonia.

In the second of these patents both air and steam are in excess. Cyanides are supposed to be produced, and subsequently decomposed by the excess of steam to produce ammonia. The latter, in presence of carbonic acid of the mixed gases, is supposed to form ammonium carbonate, and this is said to be decomposed by gypsum, yielding calcium carbonate and ammonium sulphate.

* Armengaud and Ertel (*ante*) both advocated the use of moderate temperatures—cherry red—and Marguerite and Sourdeval showed that baryta in presence of charcoal absorbed nitrogen at a comparatively low temperature, and that a light red or even a lower temperature is sufficient.

† This was suggested by L. Thomson in 1839. It would naturally occur to any one familiar with the old prussiate process, but the conditions are different in the two cases, and the reason for using it here is not apparent. The carbide of iron may possibly play an intermediate part in the production of cyanogen, such as Berthelot supposes to be played by C_2K_2 , as above quoted.—B.

These processes have been tried on a large scale experimentally, but are not as yet commercially successful.

J. Young, in 1884 (*Ysb. chem. Tech.*, 1887, 675), patented a process for cyanides intended to meet the difficulty hitherto encountered in the rapid destruction of the apparatus. He proposed to use magnesian limestone or other suitable basic substance for constructing the retorts.

Siepermann (Eng. Pat. No. 16,046, Dec. 6, 1884), 1887, obtains cyanates by passing ammonia over a mixture of barium carbonate with alkaline carbonates. For cyanides he adds coal-powder to the mixture. He gives the results of experiments, showing the effect of temperature upon the production of cyanides. Excessively high temperatures yielded poorer results than a moderate red heat.

Dickson, in 1887 (U. S. Pat. No. 370,768, O.G. 4, 1887), patented a process for production of cyanides and ammonia by injection of a mixture of air, steam, coal-dust, or hydrocarbon vapour, and powder of alkalis or alkaline earths into a chamber heated by the combustion of the injected, finely divided fuel alone. His method also contemplates the maintaining of pressure (one to three atmospheres) in the furnace.

(To be continued).

CORRESPONDENCE.

GLASER'S "ALCOHOL METHOD" FOR DETERMINATION OF OXIDE OF IRON AND ALUMINA IN PHOSPHATES.

To the Editor of the Chemical News.

SIR,—Your correspondent, "A.I.C." (*CHEM. NEWS*, vol. lxii., p. 73), will find that by adding a solution of ammonia, in excess, before commencing the evaporation of the alcohol, and again a slight addition after the alcohol has been expelled, and the solution then boiled, the difficulties he has met with will be overcome. The precipitate of phosphate of iron and alumina will now be completely separated, and without difficulty, through a filter connected with a vacuum.

Your correspondent writes:—"A number of trials have convinced me of the superiority of the 'alcohol method' as compared with the old process involving the use of acetic acid." He is quite right; and if other chemists in this country also came to this conclusion, the remark that "no two English chemists ever agree in their iron and alumina returns" would probably never have recently been made to us by one of the leading superphosphate manufacturers.

The advantage of the "alcohol method" for determining iron and alumina in phosphates is, that it enables this estimation to be correctly done with comparative simplicity and rapidity: whereas the older methods only yield *correct* results after an expenditure of time and care that few inorganic determinations require.—We are, &c.,

E. F. TESCHEMACHER and J. DENHAM SMITH.

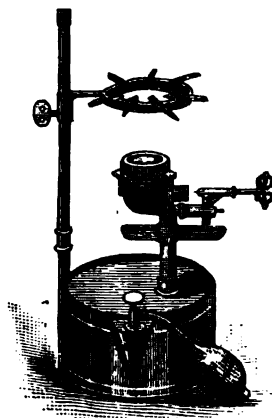
1, Aubert Park, Highbury, N.,
London, Aug. 11, 1890.

OIL GAS LAMP.

To the Editor of the Chemical News.

SIR,—In the *CHEMICAL NEWS*, vol. lxi., p. 244, a scheme is described for manufacturing gas in laboratories not provided with a supply of coal gas. The writer was probably not aware that an excellent and compact lamp is sold which virtually does the same thing, without, however, the charcoal furnace to vaporise the liquid fuel; this

being done by an ingenious adaptation of the gas flame itself. It is known as the "Dangler Lamp," and is made by the Dangler Stove and Manufacturing Company, of Cleveland, Ohio. They cost about £1, and being only 7 inches in diameter and 18 inches high, go conveniently on the laboratory bench. Having no gas supply at hand, I ordered a couple when establishing this laboratory, and have found them in every respect *superior* to gas. Fusions



Dangler Lamp.

are made with the greatest ease, and no trouble has been experienced in igniting calcium oxalate to CaO, or magnesium ammonium phosphate to $Mg_2P_2O_7$. They are started in a few minutes and require scarcely any attention, and as there is no foot blower to attend to, one can be engaged in other work while a precipitate is being ignited. Here we use gasoline (of 74° to 90° flash) as fuel, but if that could not be obtained I do not doubt that any other light oil would answer equally well.

They can be purchased from Messrs. Eimar and Amend, 205, Third Avenue, New York, but I do not know whether any English houses keep them; if not, it would be well worth their while to do so.—I am, &c.,

BEVINGTON H. GIBBINS.

Ocala Mining Laboratory,
Ocala, Fla., July 23, 1890.

P.S.—I may add that I am in no way interested in the sale of these lamps, only being anxious that other chemists may know of this exceedingly useful laboratory arrangement, and friends to whom I have mentioned it in England suggested my writing to the *CHEMICAL NEWS* on the subject.—B. H. G.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 4, July 28, 1890.

The Typical Hydrate of Neutral Aluminium Sulphate.—P. Marguerite-Delacharlony.—The author has analysed a natural aluminium sulphate from Bolivia, partly crystalline and partly amorphous. The former portion answers to the formula $Al_2O_3 \cdot 3SO_3 \cdot 16HO$, whilst the amorphous incrustation contains subsulphates derived from the decomposition of a neutral sulphate. The formula $Al_2O_3 \cdot 3SO_3 \cdot 18HO$ does not correspond to any definite real body.

Rotatory Power of Camphor Dissolved in Various Oils.—P. Chabot.—The molecular rotatory power of camphor varies very little, dilution in the camphorated oils increasing as the dilution is greater. This is contrary to what has been observed in the other solutions of camphor.

On the Lithium Malonates.—G. Massol.—A thermochemical paper, treating of the neutralisation heats of the acid and neutral lithium malonates.

On Silver Malonates.—G. Massol.—This salt, $C_6H_3O_8Ag_2$, is obtained by the double decomposition of potassium malonate and silver nitrate. It is a white or faintly yellowish power formed of fine microscopic needles which blacken on exposure to light. When dried in the open air, but in the dark, it yields 67.11 per cent metallic silver. If heated it blackens slightly, takes fire, and burns with brisk deflagration, leaving a residue of metallic silver. It is slightly soluble in water; at 20° 1 equiv. dissolves in 559 litres of distilled water, absorbing -9.8 cal. The formation of this salt by double decomposition is accompanied with a liberation of heat.

Researches on Dispersion in Organic Compounds (Fatty Acids).—Ph. Barbier and L. Roux.—The authors present the results of their studies on the dispersion of the fatty acids. They have examined from this point of view the normal homologous acid from the formic to the pelargonic acids, besides two abnormal acids, the isobutyric and the isovaleric. The dispersive powers of the normal fatty acids increase with their molecular complication. Formic acid alone presents an irregularity, which disappears if, instead of the dispersive

powers, B , we consider the specific dispersive powers $\frac{B}{d}$.

The specific dispersive powers of the isomeric compounds are almost identical, those of the non-normal acids being slightly inferior to those of the normal acids. The differences between the successive values of the molecular

specific dispersive powers $\frac{B}{d}M$ are approximately

constant, and about equal to 7.8, which permits us to represent the variation of the specific dispersive power as a function of the molecular weight by a relation of the

form $\left(\frac{B}{d} - b\right)M = a$, in which we have $a = -11.515$, $b = 0.5625$.

Presence of Furfural in Commercial Alcohols.—L. Lindet.—All commercial alcohols are not accompanied by furfural, which is a mere accidental impurity, and should be struck out from the list of the products of normal fermentation.

Contributions to the Study of Artificial Musk.—Albert Bauer.—The artificial musk is a trinitrobutyltoluene. It crystallises in fine white needles, fusible at 96–97°, insoluble in water, but soluble in alcohol and ether. Its solutions have powerful odour of musk, and may be substituted for natural musk in many of its applications in perfumery. It is evidently distinct from natural musk, which is a resin not containing nitrogen. Artificial musk is not poisonous, as the author has ascertained by experiments on rabbits. The homologues of isobutyltoluene behave like the latter, and yield trinitroderivatives of a strong musky odour.

Revue Générale des Sciences Pures et Appliquées.

Vol. i., No. 13, July 15, 1890.

The Rare Earths.—E. Demarcay.—In this paper the author seeks to present a summary of our present knowledge of the rare earths rather than to bring forward any new facts or to present any novel conclusions. He admits that the "radiant matter test" of Mr. Crookes is far more sensitive than the "reversion process" of M. de Boisbaudran. He considers that the red phosphorescence of aluminium is due to

traces of chrome, and that the phosphorescence of yttria is in like manner occasioned by traces of foreign matter rather than to its consisting of a number of distinct elements. He contests the hypothesis of meta-elements, and concludes that in the group of rare earths we have to do not with exceptional bodies, but with bodies which our ordinary methods are unable to separate. He refers to the observation of Bunsen and Becquerel, that salts present variable absorptions according to the directions taken by the luminous rays in a crystal. M. Becquerel thinks that in (old) didymium the groups of bands characterise as many different elements. Hence there would be in (old) didymium about 10 elements, 4 of which would form components of praseodymium. The same *savant* has shown that when we examine a series of didymium compounds the bands of one and the same group are displaced by the same quantity in passing from one salt to another ($\lambda - \lambda' = \lambda_1 - \lambda'_1 = \lambda_2 - \lambda'_2 = \&c.$), a quantity which varies from group to group for the same combinations. M. Demarcay thinks that for the present any conclusion is premature. He declares that concerning gadolinium Mr. Crookes has brought forward a "series of contradictory opinions." Concerning dysprosium, Mr. Crookes is of opinion that this element contains at least another. Lecoq de Boisbaudran informs M. Demarcay that he shares this opinion, and that he restricts the name dysprosium to an element characterised by the band $\lambda - 47.5$. The researches of H. Krüss and Nilson are unfavourably criticised. Mr. Crookes declares that he has obtained results contradictory of those of these *savants*, and M. Demarcay confirms absolutely the results of Mr. Crookes. The author says groups of rare earths seems likely to be the means of an important progress in our classification of the simple bodies. Of all those hitherto attempted there is nothing sound except perhaps the linear series of Newlands, which may be regarded as a first approximation.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 54.

Falsification of Commercial Olein with Linoleic Acid.—MM. Grandval and Valser.—The use of oleic acid, known commercially as olein, has been extended of late years both in soap-making and in the woollen trade for oiling wools before spinning. A certain number of spinners prefer it to olive oil both on account of its lower price and because it can be afterwards removed by means of soda-ash, whilst olive oil requires the application of soap. Latterly the use of oleic acid has occasioned much inconvenience. White cloths woven from yarns thus greased present stripes of an indelible yellow colour, which neither scouring nor bleaching with sulphur can remove, and which show very distinctly if the cloth is dyed with a light colour. On examining the "oleins" which have caused this mischief, they are found to contain a large proportion of linoleic acid. For some years the more liquid portion of recent animal fats has been melted out at a gentle heat and sold for the manufacture of margarine, whilst the more solid parts have been sold to candle-makers, but they have been found difficult to manipulate and purify. Hence linsed oil has been added to the hard animal fats, and the oleic acid which is expressed from the mixture contains linoleic acid, which is much more siccative and liable to oxidation. If such oleic acid is used for greasing wool, then, if the yarns are woven immediately after spinning, no inconvenience seems to arise, but if the yarn is left for some weeks exposed to air and light without being woven it turns strongly yellow, especially on the outer parts of the folds. For the detection of the falsified oleic acid the following characters will suffice:—It is of a yellowish brown, paler than that of commercial oleic acid. Its sp. gr. is higher, varying from 0.912 to 0.919, whilst that of genuine oleic acid does not exceed 0.905. The

liquid is more consistent, and is not homogeneous, but clotty. If falsified oleic acid is heated to 50° it takes, when cold, a firmer condition, which becomes more decided each time the operation is increased. If we take 50 grms. of the suspected sample and add 450 c.c. of alcohol at 85° there is produced on shaking a mirror-like precipitate, whilst ordinary oleic acid dissolves completely. If mineral oil, resin, or paraffin is mixed with the oleic acid there is also formed a deposit insoluble in alcohol. If a thin layer of the fraudulent oleic acid is placed upon a slip of lead, scraped quite clean, and some pure oleic acid is put upon a similar slip of lead for comparison, the next day the impure acid will be more or less resinified, whilst the pure acid will be scarcely altered. If some drops of falsified oleic acid are mixed with an equal vol. of soda-lye, an intense yellow colour is produced; pure oleic acid, if similarly treated, merely takes a greyish tint.

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By PROFESSOR E. HJELT,
of Helsingfors.

Translated from the German by J. BISHOP TINGLE,
Ph.D., Assistant in the Laboratory of the Heriot
Watt College, Edinburgh.

In this work the fundamental theories of organic chemistry are presented in a clear and concise form, and their application is fully illustrated by examples. The relations between the constitution of compounds and their chemical and physical properties are prominently exhibited. A considerable number of general reactions are discussed and explained; in all cases these are classified according to the results; for instance, reactions involving oxidation are grouped together, and examples are given of the effects of oxidation on different classes of compounds: a lucid account is also given of the special application of particular oxidising agents.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1604.

A NEW METHOD AND DEPARTMENT OF CHEMICAL RESEARCH.

By Dr. G. GORE, F.R.S.

In the *Philosophical Magazine* of May last the author has published an account of an experimental research under the above title in which he has shown that some of the chief physical and chemical properties of substances may be to a large extent represented by means of geometrical curves.

The method employed in this research was to take a small glass vessel containing 155 grains of distilled water at atmospheric temperature, immerse in the water a voltaic pair composed of an amalgamated zinc wire and sheet of platinum, connect the couple in series in the same circuit with a suitable galvanometer and thermoelectric pile, and measure by the method of balance the electromotive force of the combination. A small but known weight of a given halogen, acid, or salt was then dissolved in the water, and the electromotive force again measured; a second quantity of stronger solution was then taken, and a second measurement made; and so on until the degrees of electromotive force of about twenty different strengths of solution had been obtained. The results were then plotted on equally divided scales, with the electromotive forces as ordinates to the quantities of substance as abscissæ, and a curve of the degrees of electromotive force for equal variations of strength of solution was thus obtained. The electromotive force obtained with water was =1.127 volts, and the curve graphically given of each substance in the above publication, except in one instance, commences at that number. Curves of electromotive force were also obtained by several other methods, viz., *b*, by varying the strength of the solution at one metal only; *c*, by varying the temperature of the solution at both metals; and *d*, by varying the temperature at one metal only.

The thermo-electric pile employed was one formed of about 300 pairs of iron and german silver wires (see *Proc. Birm. Phil. Soc.*, vol. iv., p. 130; *The Electrician*, 1884, vol. xii., p. 414), and the galvanometer was an ordinary astatic torsion one of 100 ohms resistance.

In consequence of the following circumstances, very little error or inconvenience was caused by polarisation:—1. All the measurements were made at the null point when no perceptible current was passing; 2. By experience in working, the null point could be almost instantly attained; 3. The metals were immersed only a very short period of time; 4. The zinc was cleaned each time before immersion; 5. The platinum was washed each time, and heated to redness occasionally; 6. To test whether the couple remained unchanged it was occasionally balanced in distilled water by a similar one in distilled water.

Suitable strengths of solution were employed; the range of strength varied according to the degree of chemical and voltaic energy of the substances, and the strength was smaller in proportion as the substance was more energetic. The accompanying table gives the ranges of strength used with the different substances; in each case in section "a" the quantity of water employed was 155 grains.

The curves obtained with chlorine, bromine, and iodine show:—1. An increase generally of electromotive force attending increased strength of solution. 2. A much greater increase caused by the first amount of substance added than by the subsequent additions. 3. A gradation of degree, both of first increase and of maximum electro-

a. Strength of solution varied at both metals:—

	Grains of substance.
Cl, Br, and I	0.001 to 0.01
HCl, HBr, HI (<i>weak</i>)	0.001 " 0.01
HNO ₃ , H ₂ SO ₄ (<i>weak</i>)	0.001 " 0.01
H ₂ SO ₄ , at 60° C.	0.001 " 0.01
HCl, HBr, HI (<i>strong</i>)	0.1 " 1.0
HCl, with Cd as positive metal	0.1 " 1.0
KCl, KBr, KI	0.1 " 1.0
KBr, at 60° C.	0.1 " 1.0
NaCl, NaBr, NaI	0.1 " 1.0
KClO ₃ , KBrO ₃ , KIO ₃	0.7 " 1.7
K ₂ SO ₄ , Na ₂ SO ₄	0.1 " 1.0
KCl+KI, KCl+NaCl	0.1 " 1.0
Isomeric solutions	0.01 " 0.1

In each of the sections "*b*" and "*c*" the quantity of water employed was 465 grains.

b. Strength of solution varied at one metal only:—

KBr, NaCl, KCl 0.1 grain.

c. Temperature of solution varied at both metals:—

HCl, from 10° to 100° C. .. 0.03 grain.

d. Temperature of solution varied at one metal only:—

Cold Zn and hot Pt from 17°
to 100° C. 39 grains of KCl.
Cold Pt and hot Zn from 15°
to 100° C. 39 " "

motive force in the three curves, varying inversely as the magnitudes of the atomic weights of the substances. 4. A general similarity of form, sufficient to show a graduated degree of likeness. 5. A sufficient degree of difference of form to characterise each individual substance.

Those given by the weak solutions of hydrochloric, hydrobromic, and hydriodic acid show:—1. That the union of hydrogen with the halogens greatly diminished the electromotive force. 2. A feeble increase of electromotive force, greatest at the commencement, especially with hydrochloric and hydrobromic acids, attending increased strength of the solution. 3. A less degree of family likeness than in the curves of the halogens. 4. The substance of largest molecular weight gave the smallest increase of electromotive force. 5. Each substance gave a characteristic curve. The solutions were too weak to fully develop the characteristic forms of the curves.

The curves given by weak solutions of nitric and sulphuric acid are:—1. Very different from those of the halogens, and show very much smaller degrees of electromotive force. 2. Their differences from those of hydrochloric, hydrobromic, and hydriodic acid of the same range of strength are also quite conspicuous. 3. They are sufficiently unlike to be characteristic of each substance and to be clearly distinguishable from each other. The solutions were, however, too dilute to fully show the characteristic forms.

By comparing the curve given by dilute sulphuric acid at 60° C. with that given by the same range of strengths of the solution at 14° C., we find that a rise of temperature caused a general increase of electromotive force, greatest at the commencement, and quite sufficient to distinguish the one curve from the other. The difference would probably be much greater with stronger solutions, as was subsequently found with solutions of potassium bromide at 18° C. and 60° C.

The curves given by the strong solutions of hydrochloric, hydrobromic, and hydriodic acids show:—1. A general increase of electromotive force attending gradually increased strength of liquids. 2. A much larger increase produced by the first amount of substance added than by the succeeding ones. 3. A gradation of degree of general increase of such force varying inversely as the magnitudes of the molecular weights of the substances. 4. A family likeness of the curves with sufficient difference of form to

characterise each individual substance. By comparing these curves with those obtained with the solutions of one-hundredth the degree of strength, we find with the stronger solutions:—1. A much greater increase of electromotive force, both on the addition of the first amount of the substances and by the subsequent additions. 2. A more distinct relation of those increases to the magnitudes of the molecular weights of the substances. 3. Much more characteristic curves. 4. A much greater irregularity of form; this greater irregularity of form was a genuine effect.

By comparing the curve obtained with cadmium as a positive metal with that obtained with zinc in the same series of solutions of hydrochloric acid, we find:—1. Quite a different form of curve. 2. A smaller increase of electromotive force on adding the first portion of acid. 3. A general decrease of that force by the further addition of acid. 4. A curve characteristic of the metal and acid.

The curves obtained with zinc in solutions of chloride, bromide, and iodide of potassium show:—1. A much greater increase of electromotive force caused by the first amount of substance added than by the subsequent ones. 2. A gradation of degree of first increase and of maximum electromotive force, varying inversely as the magnitudes of molecular weight of the substances. 3. Large differences of form, characteristic of each individual substance. 4. The substitution of potassium for hydrogen in the corresponding acids lowered the electromotive force in all three cases, and the amount of this reduction varied inversely as the magnitudes of the molecular weights of the substances; the union of potassium with the halogens had similar effects, but in much greater degree.

By comparing the curves given by the same series of solutions of potassium bromide at 18° C. and 60° C., we find considerable differences:—1. A greater unlikeness of general form. 2. A general and large diminution of electromotive force at the higher temperatures. 3. A much smaller increase of that force on the addition of the first portion of the substance. The results support the conclusion that potassium bromide behaves to a certain extent like a different substance at such different temperature.

The curves obtained with chloride, bromide, and iodide of sodium show:—1. A general increase of electromotive force by increase of dissolved substance. 2. A great difference of form, and a strongly characteristic curve in each case. 3. The substitution of sodium for potassium in each salt considerably diminished the degree of electromotive force produced by the first addition of the substance, and the amount of this reduction varied inversely as the molecular weights of the salts. The curves are widely different in form from those of the corresponding salts of potassium, and this is, no doubt, due to the difference of metallic base; in each group, however, the curve of the chloride intersects that of the bromide.

The curves yielded by the chlorate, bromate, and iodate of potassium were very feeble, and very different from those given by the chloride, bromide, and iodide, and show:—1. A striking similarity of general form, probably due in a large degree to the general feebleness of the action as well as to analogy of chemical composition. 2. A very small increase of electromotive force in each case on adding the first portion of substance, and on subsequent additions, and the amounts of these increases varied directly as the magnitudes of the molecular weights of the salts. 3. A sufficient degree of difference to characterise each substance. 4. The chemical union of oxygen with the three corresponding halogen salts to form these compounds, greatly reduced the electromotive force in each case. Increased complexity of composition was attended by decreased voltaic energy (see "Loss of Voltaic Energy of Electrolytes by Chemical Union" (*Proc. Birm. Phil. Soc.*, vi., p. 225; *CHEMICAL NEWS*, 1889, lix., p. 183); this is a general result.

The curves yielded by the solutions of sulphate of po-

tassium and sulphate of sodium were much alike, due to their being those of closely allied salts of the same acid; but were also different in consequence of difference of their metallic bases. They are each considerably unlike those of the halogen salts of the same metals.

Comparisons of the curves obtained with solutions of mixtures of equivalent weights of KCl+KI and of KCl+NaCl showed:—

1. That each curve was strikingly unlike in general form each of those of the constituent salts of the mixtures, and the form is not in either case an average of that of the two.

2. Each of them shows a great reduction of electromotive force, due to the chemical union of the two dissolved salts (*Ibid.*; also "Examples of Solution Compounds," *Proc. Birm. Phil. Soc.*, vii., p. 33; *CHEMICAL NEWS*, lxi., p. 172; *Proc. Roy. Soc.*, xlv., p. 265).

3. In each case an increase of strength of solution is attended by an increase of electromotive force.

4. The two curves are each characteristic of the particular dissolved "solution compound."

The relative amounts of voltaic energy, as tested by the "voltaic balance," separately before chemical union, were KCl=699,803, NaCl=207,589, and KI=16,361; and after the union those of the compounds were KCl+KI=7,571 and KCl+NaCl=5,959 (see "Relative Amounts of Voltaic Energy of Aqueous Solutions," *Proc. Roy. Soc.*, xlv., p. 442; *Proc. Birm. Phil. Soc.*, vii., p. 42).

In a research "On the Molecular Constitution of Isomeric Solutions" (*Phil. Mag.*, Oct., 1889, p. 289) the author has shown that aqueous isomeric electrolytes yield different amounts of voltaic energy with a zinc-platinum couple. In the present case was employed an unstable solution "A," having a composition represented by the formula $\text{Na}_2\text{SO}_4 + 2\text{HNO}_3$, and yielding by the "voltaic balance" method, an average voltaic energy of 77.446; and its stable isomer, "B," represented by $2\text{NaNO}_3 + \text{H}_2\text{SO}_4$, and yielding 32.722. The curves given by the two series of strengths of these mixtures were largely different in form; they showed the considerable differences of molecular and chemical constitution of the two liquids, and enabled the two mixtures to be readily distinguished. As the unstable liquid "A" is easily changed into the stable one, "B," by heating it to nearly 100° C. in a stoppered glass flask during fifteen minutes, and then would give the curve of "B," it is evident that the method of examining aqueous solutions by means of their curves of electromotive force is applicable for detecting and measuring chemical and molecular changes in them (see "A Method of Examining the Rate of Chemical Change in Aqueous Solutions" (*Proc. Roy. Soc.*, xlv., p. 440).

The curves obtained in solutions of potassium bromide or sodium chloride, by varying the strength of the liquid at one metal only of the voltaic couple, showed:—

1. That the variation produced a large and irregular effect upon the electromotive force at the surface of the zinc, but scarcely any such effect at that of the platinum.

2. That when such variation of strength is made at both metals simultaneously, the effect upon the electromotive force, and consequently upon the form of the curves, is nearly wholly due to changes occurring at the surface of the zinc, and but little to such changes at the platinum.

The curves which resulted from gradually raising the temperature of dilute hydrochloric acid from 10° to 100° C. at both metals simultaneously showed that a regular variation of temperature produced an irregular change of electromotive force. It is probable that the curve thus obtained is characteristic of the substance, and would be different with every different substance and degree of strength of its solution.

By raising the temperature of the solution of potassium chloride from 15° to 100° C. at each metal separately, two curves of quite different forms were obtained. The greatest variation of electromotive force was at the zinc,

and was = 0.103 volt, whilst that of the platinum was only = 0.04 volt. Each of these curves would probably be characteristic of the particular dissolved substance and degree of strength of its solution.

General and Theoretical Considerations.

The evidence obtained by this research shows:—

1. That every different electrolytic substance, when in aqueous solution, gives, by varying the degree of strength of its solution (or by varying its temperature), a different curve of electromotive force.
2. That this curve is characteristic of the substance.
3. That under these conditions, substances which constitute a recognised chemical group yield a series of curves which usually exhibit a gradation of likeness of form.
4. That the degrees of electromotive force of such a group usually vary in magnitude inversely as the amounts of the atomic or molecular weights of the substances.
5. That a much greater increase of electromotive force is usually caused by the first amount of substance added to the water than by the subsequent amounts.
6. That the chemical union of two substances to form a soluble salt is attended by a definite decrease of electromotive force and a definite change of form of curve.
7. That the substitution of one halogen acid or metallic base for another in the composition of a soluble electrolytic salt, is accompanied by a definite amount of change of that force and of the form of its curve; and it will probably be possible to trace, by means of these changes, the presence of each halogen acid and metal in the various solutions of its salts.
8. That isomeric solutions of electrolytic substances give different curves under the same conditions, and may thus be distinguished from each other.
9. That molecular and chemical changes and their rates, in electrolytes, may be examined and measured by this method.
10. That if the solutions of the substances are too weak the characteristic forms and differences of the curves are not fully developed, and if they are too strong the measurements of electromotive force are more difficult to make. As the measurements were made at the null point when no current was passing, the curves represent the electromotive forces and molecular motions which exist under that condition; when the current passes the molecular movements are greatly altered.

The changes of electromotive force and form of curve obtained:—1st, by the same variations of strength of the same solution at two different temperatures; 2nd, by varying the temperature of a solution without changing its strength; and 3rd, by varying its temperature at the positive metal only, or at the negative one only, support the general view that each substance becomes more or less a different substance at each different temperature, and that the degrees of property of each substance at different temperatures are practically infinite in number.

The results in general support the kinetic theory that the most fundamental attribute of matter is motion, that a mass of matter is a mass of motion, that each substance consists essentially of a collection of molecular motions, and that the chief properties of bodies are consequences of such motions. Changes of volta electromotive force are now generally recognised as being due to those motions, and as being disturbances of the universal ether which pervades all bodies and all space. Each degree of such force may also be regarded as a concrete result of an extensive series of molecular vibrations of extremely varied degrees of amplitude; this series being characteristic of the particular material combination producing it, analogous to the collection of vibrations producing a beam of light of a particular burning substance. The curves represent, in addition, the changes in amount of these collective motions; and by observing these changes

in a single substance under a sufficient variety of conditions, a more or less complete graphic delineation of them as representing that particular substance might be obtained. When we are able to fully interpret the language or meaning of these curves we shall learn a very great deal respecting the internal motions and changes of substances, and the conditions of conversion of potential into kinetic energy.

As each curve is a geometrical and quantitative representation of a series of such changes, a complete collection of such curves, yielded by all kinds of aqueous solutions, would constitute an extensive system of representations of the molecular motions of substances somewhat like that of the luminous spectra of bodies; and the magnitudes and harmonic relations of the degrees of electromotive force represented by the curves will form a very large basis of study for mathematicians, something like the spectra of bodies now afford. The entire subject appears to be nearly as large as that of spectrum analysis, and is not altogether unlike it.

The whole system of curves may be viewed as being in some respects analogous to the absorption spectra of liquids, and in a less degree to the spectra of gases. The relations between the different curves are probably more complex than those between the spectra of liquids, because the electrodes take part in the action; and still more complex than those between the spectra of gases, because of the influences of the solvent and of the electrodes, and because each dissolved substance is in the liquid state, and under the influence of cohesion.

As the magnitudes and forms of the curves are manifestly related to the atomic and molecular weights of the dissolved substances, they are doubtless also related to the periodic series, and in this direction a study of them by mathematicians will lead to the acquisition of new knowledge. And as they reveal the kinetic changes which isomeric and other substances undergo when they pass from one state of chemical equilibrium to another in cases of chemical union, substitution, decomposition, &c., they are evidently related very intimately to Newton's third law of motion.

With regard to the latter suggestion, in several researches (see "Relative Amounts of Voltaic Energy of Electrolytes," *Roy. Soc. Proc.*, 1888, xlv., p. 266; *Proc. Birm. Phil. Soc.*, vii., p. 43; "On Loss of Voltaic Energy of Electrolytes by Chemical Union," *Ibid.*, vi., p. 225; "Examples of Solution Compounds," *Ibid.*, vii., p. 33; *CHEMICAL NEWS*, lxi., 172), the author has largely shown, by means of the "voltaic balance" method, that chemical union in definite proportions by weight of substances whilst in aqueous solution together is apparently universal; that elements unite with elements, with all kinds of acids, and with all classes of acid, neutral, and basic salts; that acids unite with acids, each with every other one, and each acid with every salt; and salts with each other in almost endless variety; and apparently that all kinds of dissolved chemical compounds, with but few, if any exceptions, unite together more or less distinctly in those definite proportions indiscriminately and without limit of kind, provided no separation of substance by precipitation or otherwise occurs. Also, by repeatedly doubling the molecular weight of a "solution compound" by successive additions to it of other dissolved substances of equal chemical value, each addition producing a new state of chemical equilibrium, in which chemical action and reaction are equal, he has by the same method shown that chemical union of substances whilst in aqueous solution extends to large aggregates of molecules of the most varied kind and of considerable degrees of complexity (*Proc. Birm. Phil. Soc.*, vi., p. 225; *CHEMICAL NEWS*, lxi., p. 183). This universality of chemical union of substances whilst in solution together indicates the existence of an equally general cause of such union, and that cause must be a molecular one.

"The theory most consistent with these facts is a

kinetic one, viz., that metals and electrolytes are throughout their masses in a state of molecular movement. That the molecules of these substances, being frictionless bodies in a frictionless medium" (viz., the universal ether), "and their motion not being dissipated by conduction or otherwise, continue in motion until some cause arises to prevent them. That every different metal and electrolyte has a different class of motions, and that the molecular motion of each substance varies at a different rate by rise of temperature." This theory has been employed by the author to explain certain phenomena in electrolytes (see *Roy. Soc. Proc.*, 1883, xxxvi., pp. 54, 55). "In accordance with this theory, chemical action is an effect of molecular motion, and is one of the modes by which that motion is converted into electric current." "Those statements are also consistent with the view that the elementary substances lose a portion of their molecular activity when they unite to form acids or salts, and that electrolytes have usually a less degree of molecular motion than the elements of which they are composed" (*Ibid.*).

A kinetic theory must agree with mechanical laws; we cannot create motion or energy; all motion arises from pre-existing motion, every efficient cause of kinetic change is a kinetic one; the immediate source of all chemical change is the latent molecular motion of the combining or mutually acting substances. As neither mere difference of substance, nor union in definite proportions by weight, is in itself an active influence, neither can it be the immediate kinetic cause of chemical change; but as both these circumstances invariably attend chemical union, and no such union occurs without them, we may conclude that they are necessary conditions of the union.

By adopting the above theory, "that electrolytes are throughout their masses in a state of molecular movement, that the molecules of these substances, being frictionless bodies in a frictionless medium, and their motion not being dissipated by conduction or otherwise, they continue incessantly in movement until some cause arises to prevent them," and associating it with Newton's third law of motion, viz., that "the actions of bodies upon one another are always equal and in opposite directions," we are driven to the inference that what we term "chemical affinity," or the immediate active cause of chemical union, is latent or potential molecular motion and the mutual impact and momentum of the molecules of the uniting substances. When two dissolved substances are brought by admixture of their solutions into mutual contact, a portion of the molecular motion of the one substance is neutralised by an equal amount of opposite motion of the other, and the two portions are converted into free heat, electric current, or other form of energy, and the molecules thus brought into nearer proximity retain their new positions and distances; this agrees with the usual evolution of heat, loss of voltaic energy, depression of electromotive force, and frequent increase of density, which occur during chemical union. According to this view, every dissolved chemical compound is an instance of balanced molecular motion, and it is the neutralised portions of motion which escape as heat and electric current. How far there is any originality in these ideas the author leaves to other persons to decide.

Many of the facts evolved by the several researches referred to point towards the conclusion that measurements of volta electromotive force and voltaic energy are essentially measurements of "chemical affinity" between the negative dissolved substance and the positive metal. An analogous idea has already been suggested by other investigators. E. F. Herroun, adopting a view of Helmholtz's, has inferred that "the electromotive force of a voltaic cell is a measure of the actual transformation of free energy," and concluded that it "furnishes a more accurate measurement of the free energy, and therefore of true chemical affinity, than data derived from calorimetric observations" (*Phil. Mag.*, 1888, vol. xxvii., p. 230).

The amounts of voltaic energy lost by two substances during their act of chemical union clearly indicate to a large extent the quantities of opposite molecular motion neutralised by their union. For instance, a much larger amount of such motion is neutralised by the union of sodium with chlorine to form sodic chloride than by that of hydrogen with chlorine to form hydrochloric acid, and, no doubt, by investigating the losses of electromotive force and voltaic energy attending the chemical union of substances in aqueous solution, we may learn a very great deal respecting the quantitative relations of "chemical affinity" between metals and electrolytes; but a great obstacle to making accurate measurements of such "affinity" by this method is the unmeasured portion of energy lost by "local action." It may be further remarked that, disregarding "local action," this chemical union and neutralisation of opposite molecular motions only occurs whilst the circuit is closed, and that at the instant of closing the circuit, potential energy is converted into kinetic energy, and a multitude of electromagnetic waves of varied lengths are generated and radiated into space; the conversion of energy, therefore, in this kind of case, depends upon closing of the circuit.

The results obtained by varying the strength or the temperature of the liquid at each metal separately support the conclusion that, in an ordinary voltaic cell, nearly the whole of the energy is due to action at the zinc, and but little to that at the platinum; and that the latter metal acts nearly wholly by obviating the greater counter electromotive force which would occur by using a more corrodible metal, and by diminishing the resistance which a less conducting substance would offer. The mere absence of an obstacle to a change cannot be an active cause of that change, and any substance which takes an essential part in any physical or chemical action, and (like the platinum plate) remains exactly the same in every respect after the action as it was immediately previous to it, cannot have been a real cause of that action, or of any loss or gain of energy attending it. The presence of the negative metal is only a static permitting condition; it enables, without any expenditure of energy on its own part, the opposite potential molecular motions of the positive metal and the negative constituent of the liquid to neutralise each other and be converted into voltaic current.

The method described in the paper is not merely a technical one of detecting substances, nor is it specially fitted for such a purpose; but it is an extensive new department of chemical and molecular research, and a general system of representation by means of geometrical curves, not only of individual substances, but of some of the fundamental changes of molecular motion of substances which are inseparably related to their chief chemical properties, and it will in this way supply mathematicians with a new and extensive series of facts, representing in terms of electromotive force, the degrees of voltaic chemical action of metals and electrolytes upon each other. Some of the chief uses of it as a method of research will be to examine the molecular structure and chemical composition of substances, to detect differences and changes in them caused by heat, light, chemical union, substitution, decomposition, &c., and to detect and measure molecular and chemical differences in isomeric liquids. It may be used to detect and measure the changes gradually produced by light and heat in chlorine-water and bromine-water, the influence of light upon nitric acid, the degrees of retarding effect of coloured glass screens, &c., upon various chemical changes caused by light, the gradual oxidation of a solution of sulphurous anhydride by exposure to air, the spontaneous decomposition of aqua regia, the rate of decomposition of a solution of potassic iodide by chlorine-water, the speed of displacement of one acid by another, &c. The examples given and researches suggested are sufficient to indicate the extensive applicability of the method.

CHEMICAL COMPOSITION OF THE OILS OF WINTERGREEN AND BIRCH, AND THE CHARACTERS OF THE SYNTHETIC OIL OF WINTERGREEN.

By Prof. Dr. FREDERICK B. POWER,
University of Wisconsin.

(Concluded from p. 77).

III. *Artificial or Synthetic Oil of Wintergreen.*—The physical properties of this oil, as manufactured by Messrs. Schimmel and Co., of Leipzig, and kindly furnished me by Messrs. Fritzsche Bros. of New York, have already been described. In connection with its chemical composition it therefore only remained to determine whether it contained any benzoic acid, since Messrs. Trimble and Schröter have made the statement, which has become widely circulated, that the salicylic acid separated from "a representative sample" of the artificial oil of wintergreen examined by them was contaminated with about 15 per cent of benzoic acid. On the basis of this assertion they take occasion to condemn the artificial oil of wintergreen, and to discountenance its recognition by the Pharmacopœia, which the writer in a former paper* had suggested, by the following expression of opinion:—

"In view of the fact that the oil of birch has in part displaced that of wintergreen, Dr. Squibb (*Ephemeris*, Oct., 1887, p. 954) nearly two years ago made some remarks about the similarity of the three, suggesting that oil of birch should be called by its correct name, and that the Pharmacopœia, by its present definition, is lending its authority to perpetuate the error. These statements have since called forth from others the recommendation that the artificial oil should be made official at the next revision of the Pharmacopœia. How far this would be undesirable may appear on examining the following analysis of a representative sample of the commercial artificial product, and reflecting on the present difference between this and either of the natural oils, and the still greater difference that would naturally follow the recommendation of the artificial methyl salicylate by the Pharmacopœia. If it is not a pure compound now, when it is competing for recognition, what would it degenerate to if it should become established by the recommendation of the Pharmacopœia?"†

Although Messrs. Trimble and Schröter have been very careful not to mention the name of the manufacturer of what they term a "representative sample" of this product, it is well known that it is included among the specialties of Messrs. Schimmel and Co., who are the largest producers of it, and whose products have not only always been without reproach, but, on account of their known purity, have served as the basis of the most extended investigations in this line by the chemists of both continents.

The above assertions of Messrs. Trimble and Schröter, so far as they might be construed to apply to the product of Messrs. Schimmel and Co.'s manufacture, have naturally not failed to evoke a prompt repudiation, and the expression of their opinion on this subject, as contained in their October *Berichte*, 1889, p. 50, is in such plain and forcible language that I take the liberty of presenting a translation of the same.

"In consideration of the rare occurrence of true gaultheria oil, the proposition made some time ago in America, that the Pharmacopœia should recognise the artificial methyl salicylate in place of the natural oil, which is subject to so much adulteration, has resulted in the opposition of the American chemists, Messrs. Trimble and Schröter. These gentlemen have not only published their motives for this in American journals, but by means

of a special pamphlet, have sought to give the same the widest possible circulation."

"We can congratulate them that they have left their readers in the dark with regard to the origin of the synthetic oil of wintergreen examined by them, for if by the disguised designation 'representative sample of the commercial artificial product' they should have meant that of our manufacture, as imported and sold by our New York house, the statement of having found about 15 per cent of benzoic acid in it would have subjected them to lasting censure."

"With regard to our product, we are in the position to furnish the assurance that it does not contain the slightest trace of benzoic acid, for the salicylic acid used in its manufacture is absolutely free from benzoic acid. We have made inquiries concerning this of Dr. Kolbe, of the firm of F. von Heyden, Nachfolger, in Dresden, who supplies us with salicylic acid, and have received from him the most convincing assurance that the occurrence of benzoic acid in his salicylic acid is absolutely out of question, and also that the formation of this acid in its manufacture is impossible."

"Although the assurance from this source should really have sufficed, nevertheless, in order to ward off any possible reflection upon the character of our oil, we have taken the pains to examine the salicylic acid of our oil of wintergreen for benzoic acid, the more especially to anticipate any assertion that benzoic acid might be formed in the manufacture of the oil. We are also thus able, from our own inspection, to confirm the statement that no trace of benzoic acid exists in our oil of wintergreen."

"Every unprejudiced person will certainly agree with us when we present an energetic front against the style and method of procedure of these gentlemen. It is generally known that the synthetic oil of wintergreen has hitherto been exclusively imported by our New York house. There can therefore scarcely be a doubt but that with the designation 'representative sample of the commercial artificial product' our product was intended. We will assume, in favour of Messrs. Trimble and Schröter, that in the suppression of our name they have believed to have shown an act of consideration. If this should have been the case, we will remark that it was quite out of place. We do not need to shun the light, and shall always be capable of defending the products of our manufacture."

From a careful examination which I have recently made of the synthetic oil of wintergreen of Messrs. Schimmel and Co.'s manufacture, I can not only fully corroborate their statement that it does not contain any trace of benzoic acid, but would unhesitatingly designate it as one of the finest products of modern chemical synthesis. Why Messrs. Trimble and Schröter should designate such a compound as that examined by them as a "representative sample" of this oil, when according to their own examination of it, it must have been evident that it was a base sophistication, is perfectly incomprehensible. Their opposition to the recognition by the United States Pharmacopœia of the artificial oil on any such grounds would seem to be no more reasonable than that the Pharmacopœia should exclude all other valuable medicinal agents which are liable to adulteration or sophistication.

The benzoic acid which Trimble and Schröter state to have been found in the artificial oil of wintergreen, as also in small amounts in the natural oils of wintergreen and birch, was separated by them from the salicylic acid by treating the latter with petroleum ether, and further purifying the last crystallisations.

In my examination of the salicylic acid from the artificial oil of wintergreen and the natural oils of wintergreen and birch it seemed desirable in the first place to ascertain the relative solubility of benzoic and salicylic acids in petroleum ether. The latter was freshly rectified, and only that portion employed which distilled over between 25° and 45° C. The solubility of salicylic acid in this

* *Pharm. Rundschau*, 1888, p. 210.

† *Amer. Journ. Pharm.*, 1889, p. 403.

liquid was found to be 1 part in 935 parts at 15° C., and the acid separates from the solution on spontaneous evaporation in small colourless needles.

The solubility of benzoic acid in this liquid was found to be 1 part in 106.3 parts at 15° C., and the acid separates from the solution on spontaneous evaporation in bright pearly scales.

Not only the difference in solubility of these acids, but also their complete dissimilarity in crystalline form, as separated from the petroleum ether, therefore, prove the latter to be well adapted for the detection of benzoic acid. But since both acids are so sparingly soluble in this liquid, I sought, if possible, to bring any benzoic acid present into a smaller compass by taking advantage of the greater solubility of the latter in chloroform, which is stated to be 1 part in 6 of chloroform, while salicylic acid requires 80 parts of chloroform for solution. The acids obtained from the oils were therefore first extracted with hot chloroform, and the portion of acid crystallised from chloroform was then treated with petroleum ether. By this method, as previously stated, not a trace of benzoic acid could be detected in the artificial oil of wintergreen, and I have been equally unsuccessful in detecting it in either a pure natural oil of wintergreen or in the specimen of oil of birch which served for this examination.

Messrs. Trimble and Schroeter also announce the presence of small amounts of ethyl alcohol in the natural oils of wintergreen and birch, as based upon the iodoform reaction afforded by the methyl alcohol separated from the oils. In this connection the fact should not be overlooked that oil of turpentine, and presumably other bodies belonging to the class of terpenes, are also capable of affording iodoform. If, for example, a few drops of pure oil of turpentine be shaken with warm water, and the liquid, after cooling, be filtered through a wet filter, such a clear aqueous solution, which can contain but extremely small amounts of dissolved oil, when treated with iodine and solution of caustic alkali, will afford, on standing, a distinct crystalline precipitate of iodoform. It would therefore not seem impossible but that, in the case of the natural oil of wintergreen at least, so small an amount of a terpene might still remain associated with the methyl alcohol as would suffice to produce this reaction. I would state, however, that I have not been able to obtain any crystals of iodoform from a filtered aqueous solution of the terpene separated from the natural oil of wintergreen, nor is iodoform afforded by the hydrocarbons of ordinary petroleum.

In summing up the results of this investigation, my conclusions, as contrasted with those of Messrs. Trimble and Schroeter, may be presented as follows:—

I. The natural oil of wintergreen consists of methyl salicylate, with small amounts (0.3 per cent or less) of a terpene. The latter is a slightly yellowish, somewhat viscid liquid, having an odour, as described by Cahours, resembling that of black pepper, a specific gravity of approximately 0.940, and does not solidify or separate any solid substance at a temperature of -10° C. It deviates the ray of polarised light to the left, and cannot be vapourised without decomposition.

II. The oil of birch, when pure, consists simply of methyl salicylate, and is without action on polarised light.

III. The natural oils of wintergreen and birch are therefore neither physically nor chemically identical, although the differences are practically very slight.

IV. In the natural oils of wintergreen and birch examined by me no trace of benzoic acid could be detected, nor has sufficient evidence as yet been afforded to establish beyond doubt the presence of ethyl alcohol in these oils.

V. The artificial or synthetic oil of wintergreen, as manufactured by Messrs. Schimmel and Co., of Leipzig, and which to the writer's knowledge is at present the only commercial synthetic oil that is entitled to be design-

ated as a representative product, does not contain any trace of benzoic acid.

VI. The pure synthetic oil of wintergreen can not be distinguished from either the natural oil of wintergreen or the oil of birch by the addition of an excess of a cold solution of potassium hydrate, nor is any "disagreeable phenol-like odour" produced, as affirmed by Messrs. Trimble and Schroeter. In the case of the artificial oil the odour of wintergreen does not disappear to any greater extent than with the natural oils. On heating either of these oils with a caustic alkali the wintergreen odour is naturally destroyed, since the chemical compound to which the odour is due becomes thereby decomposed.

VII. With regard to the adoption of the title Methyl Salicylate, and the recognition of the artificial oil of wintergreen by the Pharmacopœia, as I had suggested in a former paper, no reasonable objection can be urged. It remains, however, for the pharmacists and physicians of this country to decide, whether under the title of *Olum Gaultheria*, the Pharmacopœia should recognise the oil of birch, which is prepared chiefly in a crude manner by farmers and itinerant distillers, and is subject to adulteration with kerosene oil, or whether at least equal recognition should not be given to a pure methyl salicylate, possessing definite physical and chemical characters, and which can always be readily procured.

If any special medicinal virtues reside in kerosene oil, medical practitioners would unquestionably prefer to employ it under its proper name, and in definite or known quantities and combinations.

THE DRY ASSAY OF TIN ORES.*

PART I.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Continued from p. 79).

TABLE III. shows that the loss in tin increases if the crucibles are left too long in a very hot fire; the buttons, however, remaining free from iron.

Although the results in the naked crucible were entirely satisfactory with normal conditions of temperature and time, the chalk-lined crucible was now used to see what effect would be produced upon the assay. Assays Nos. 11, 12, 13 were made in the same way as Nos. 1 to 6, keeping the temperature reasonably low. No difference could be perceived in examining the crucible, slags, and button, except that the upper part of the crucible was more tarnished than with the naked one.

Table IV. shows an average result which does not differ much from that obtained in the naked crucible, but the assays vary as much as 0.6 per cent.

If time and temperature are increased, the difference from the results with the naked crucible becomes much greater (see Table V.).

With the exception of No. 22, all the buttons contained iron, some of the results being even then too low (Nos. 20 and 21), and others too high (Nos. 14 to 19). Apparently the lime, by entering the slag, assisted in carrying the iron into the tin. That nevertheless some tin was slagged is to be accounted for by the fact that there was not enough iron to prevent it; for metallic iron,† although if present in sufficient quantity it will precipitate the tin completely, if in too small amount will only reduce the stannic oxide to stannous oxide, which of course enters the slag.

Kerl‡ mentions the fact that by first heating with char-

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 2.

† Berthier, "Traité des Essais," vol. ii., p. 459.

‡ "Metallurgische Probirkunst, 1879, p. 483.

TABLE III.
Resulting Tin.

No. of Assay.	Total.		In button.		In scales.		In siftings.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
7.	3'320	66'40	3'25	65'00	—	—	—	—
8.	3'310	66'20	3'24	64'80	—	—	—	—
Average..	3'315	66'30	3'245	64'90	0'015	0'30	0'055	1'10
9.	3'000	60'00	2'93	58'60	—	—	—	—
10.	2'850	57'00	2'78	55'60	—	—	—	—
Average..	2'925	58'50	2'855	57'10	0'015	0'30	0'055	1'10

TABLE IV.
Resulting Tin.

No. of Assay.	Total.		In button.		In scales.		In siftings.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
11.	3'393	67'86	3'38	67'60	—	—	—	—
12.	3'373	67'46	3'36	67'20	—	—	—	—
13.	3'363	67'26	3'35	67'00	—	—	—	—
Average..	3'376	67'53	3'363	67'27	0'001	0'02	0'012	0'24

TABLE V.
Resulting Tin.

No. of Assay.	Total.		In button.		In scales.		In siftings.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
14.	3'456	69'12	3'450	69'00	—	—	—	—
15.	3'456	69'12	3'450	69'00	—	—	—	—
16.	3'446	68'92	3'440	68'80	—	—	—	—
17.	3'446	68'92	3'440	68'80	—	—	Average.	Average.
18.	3'441	68'82	3'435	68'70	—	—	0'006	0'12
19.	3'421	68'42	3'415	68'30	—	—	—	—
20.	3'391	67'82	3'385	67'70	—	—	—	—
21.	3'371	67'42	3'365	67'30	—	—	—	—
22.	3'291	65'82	3'285	65'70	—	—	—	—

TABLE VI.
Resulting Tin.

No. of Assay.	Total.		In button.		In scales.		In siftings.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
23.	3'363	67'26	3'33	66'60	—	—	—	—
24.	3'333	66'66	3'30	66'00	—	—	—	—
25.	3'253	65'06	3'22	64'40	—	—	—	—
Average..	3'316	66'32	3'283	65'66	0'002	0'04	0'031	0'62
26.	3'484	69'68	3'460	69'20	—	—	—	—
27.	3'334	66'68	3'310	66'20	—	—	—	—
28.	3'259	65'18	3'235	64'70	—	—	—	—
Average..	3'359	67'18	3'335	66'70	—	—	0'024	0'48

TABLE VII.
Resulting Tin.

No. of Assay.	Total.		In button.		In scales.		In siftings.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
29.	3'419	68'38	3'41	68'20	—	—	—	—
30.	3'339	66'78	3'33	66'60	—	—	—	—
31.	2'969	59'38	2'96	59'20	—	—	—	—
Average..	3'242	64'84	3'233	64'66	0'009	0'18	—	—
32.	3'425	68'50	3'390	67'80	—	—	—	—
33.	3'365	67'30	3'330	66'60	—	—	—	—
34.	3'205	64'10	3'170	63'40	—	—	—	—
Average..	3'332	66'63	3'297	65'93	0'001	0'02	0'34	0'68

coal alone in the crucible and then adding the fluxes, the scorification of tin will be lessened. The reason of this is apparent. If the stannic oxide be reduced to the metallic state, the fluxes then added will, upon fusion, simply assist to collect the fine particles of metallic tin into a button, and the danger that stannic or stannous oxide may be carried off in the slag is excluded. But other more powerful causes counteract the good results which might be expected from this modification of the German assay. The most important is the presence of iron in the metal. Although tin is reduced sooner than iron to the metallic state, there is no direct indication by which the assayer can know when to stop with the reduction and when to add the fluxes. If the reduction is carried too far, the iron also will be reduced and will enter the button; if not carried far enough, so that tin still remains unreduced, the main advantage of the modified method is lost. Another drawback is that the fluxes are added to the hot reduced ore in the crucible. This creates a liability to loss of ore by dusting.

In carrying out the experiments the proportions used were the same as with the regular method. The crucibles were placed in the hot fire, and, counting from the time that the ore appeared dark red, it was exposed for a quarter of an hour to a strong heat; then the fluxes were added in their regular order, and the charge heated for one hour.

The behaviour in the crucible and the general appearance of crucible and slags were not different from that with the regular method. The colour of the salt slag, however, was light green instead of dark purple; that of the borax slag dark olive-green instead of the usual lighter shade. The tin buttons did not separate well from the slag, as their surface was very uneven. In some places were slight depressions or even cavities; in others, the button was covered with small beads of metal, adhering partly to it and partly to the borax slag. Some of the buttons were bright, and more or less malleable, and free from iron; others, however, contained so much iron that they had not the usual white colour and bright appearance, and cracked when hammered flat to the size of a dime.

Two double sets of experiments were carried out, the one in a naked crucible at a normal and then at a high temperature, the other in a chalk-lined crucible under the same conditions. The results obtained in the naked crucible are given in Table VI.

The average result of assays Nos. 23, 24, 25, carried out at a normal heat, is over 1 per cent lower than that obtained by the regular method, and there is a difference of 2.6 per cent between the highest and the lowest of the results. The buttons, however, were all free from iron. Those from assays Nos. 26, 27, 28, carried out at a high temperature, show the presence of iron in quite a marked degree. There was no regularity whatever; No. 26 took up so much iron that the button weighed more than the tin obtained by chemical analysis; Nos. 27 and 28 also took up iron, and at the same time gave some tin to the slag.

The results obtained by this modified method are therefore unsatisfactory. They become still more so if the assay is carried on in the chalk-lined crucible. This can be seen from Table VII.

Of Nos. 29, 30, 31, made at a low temperature, one assay (No. 29) contained iron, and between the other two there is a difference of 7.4 per cent. This discrepancy was probably caused by the large amount of tin carried off in the slag of No. 31. Under the caption "Siftings" there is a blank. As siftings there remained in the pan a heavy brown-black slag, which, when examined in the wet way, proved to be rich in tin. The assays Nos. 32, 33, 34, carried on at a high temperature, gave buttons which were all strongly ferruginous; they also showed great irregularity. Judging from the results obtained by the modified method—Nos. 23 to 32—the preference must be given to the regular German method, although, as above

stated, it would seem rational to suppose that the loss in tin would be smaller if the black tin were reduced to the metallic state before the flux is added and the fusion begins.

Mitchell* gives a method which may be mentioned in connection with the German assay. He mixes 400 grains ore, 100 argol, 300 sodium carbonate, 50 lime, and charges in a crucible so large that it need only be half filled, then gives a cover of sodium carbonate and 200 grains of borax; heats gently, and keeps for at least twenty minutes at a dull red heat, increasing the temperature until tranquil fusion takes place.

The experiments were carried out as directed. A beautiful bottle-green slag resulted. It was as glassy as obsidian, and covered with a thin slag of a lighter green colour. The results from three consecutive assays were so discouraging that no further attempts were made in that direction. Nearly all the tin had been taken up by the slag, the only apparent reason being the intimate mixing of ore and flux.

(To be continued).

THE FIXATION OF ATMOSPHERIC NITROGEN.†

By A. A. BRENNEMAN, S.B.‡

(Continued from p. 84.)

The Formation of Metallic Nitrides.

R. WAGNER in 1857 (*Jsb. chem. Tech.*, 1857, 121) had suggested that nitrides of boron and silicon in the interior of the earth might be the source of the ammonia found in combination with boric acid in the lagoons of Tuscany, and as sal-ammoniac in volcanic exhalations. This ammonia may be a product of the action of water at high temperatures upon the above nitrides. Bunsen, however, and Rainer (*loc. cit.*) regard volcanic ammonia as of organic origin, resulting from action of subterranean heat upon fossil vegetable matter, coal, lignite, &c.

Briegleb and Geuther in 1862 (*J. pr. Ch.*, cxxiii, 228) investigated the question of the metallic nitrides. The close relation of these bodies to the cyanides renders a knowledge of them of much interest in this connection. Nitrides of magnesium, aluminium, and chromium were obtained by simply heating the metals in pure nitrogen. The temperature of combination of nitrogen with the metal seems to be near the melting-point of the latter. Magnesium nitride is a greenish yellow, amorphous mass which yields ammonia in contact with water or caustic alkalis, and yields cyanogen when heated in an atmosphere of carbonic oxide or carbon dioxide. It has the composition Mg_3N_2 .

Tessie de Motay in 1872 (*Jsb. chem. Tech.*, 1873, 279; *Ber.*, 1872, 395) announced that titanium nitride could be made to yield ammonia by the action of steam, and could then be regenerated by submitting it to a current of nitrogen and the action thus alternated successively.

Mallet in 1876 (*Proc. Am. Chem. Soc.*, i., 17) obtained magnesium nitride by the combustion of magnesium powder in a crucible with insufficient admission of air. Other nitrides, of boron, titanium, silicon, &c., have been investigated by Ufer, Uhrlaub, Wohler, Deville, and Caron (*J. pr. Ch.*, ci., 359; ciii., 230; cv., 69; cx., 248.)

Cyanogen from Oxides of Nitrogen.

Binks (R. W., vol. i., Pt. v., p. 60. Eng. Pat. No. 10,911, Nov. 3, 1845) proposed to use oxides of nitrogen or vapour of nitric acid for production of cyanides. The

* "Manual of Assaying," New York, 1881, p. 481.

† *Journal of the American Chemical Society*, vol. xi., Nos. 1-2.

‡ The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

gases were brought in contact with vapours of hydrocarbons in passing through a highly heated cylinder filled with firebrick. When the nitrogen compounds are in excess ammonia is chiefly produced, but with hydrocarbons in excess cyanides are the principal products. Crane and Jullion (*loc. cit.*) used a somewhat similar process, using, however, an excess of water-gas (hydrogen and carbonic oxide) mixed with the oxides of nitrogen and hydrocarbon vapours, and passing the mixture over a hot catalytic substance (platinised asbestos) at a temperature of 600° F.

Firman (*loc. cit.*, p. 65), and others have proposed the use of waste gases of the sulphuric acid chamber (nitrogen, oxides of nitrogen, &c.), for the same purpose.

A process suggested by Roussin in 1858 (*Comptes Rend.*, lxxvii., 875; *J. pr. Ch.*, lxxviii., 375) uses oxides of nitrogen in a different way and recalls the very early methods of Diesbach and Woodward (*ante*). With the object of converting nitrates into cyanides he made the following experiment:—Four equivalents of crude potassium acetate were mixed with three of potassium nitrate (nitre) and five of potassium hydrate or carbonate, and heated in a porcelain crucible to 350° C. The mass burned briskly, leaving a black residue, which, on lixiviation, yielded potassium cyanide and carbonate. By addition of coal powder, to make up for the deficiency of carbon in the organic acid, an increased yield of cyanide was obtained, but still short of the theoretical result. Previous reductions of the nitrate to nitrite yielded better results, and a mixture of potassium acetate and nitrite with lampblack gave 2.6 parts of Berlin blue (dried at 100° C.) to 13 parts of acetate, and an ammoniacal odour during the operation showed a loss of nitrogen. Potassium tartrate yielded little cyanide when used to replace the acetate, a fact already announced by Guibourd. Roussin suggested that a commercial process could be based on the use of crude sodium nitrate and acetate.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 19th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. J. Caird, 20, Springfield, Dundee; D. G. Clark, 44, St. John's Wood Park, N.W.; Walter Henry Coleman, 41, Poyning's Road, Junction Road, N.; Thomas Rhymer Marshall, 4, East Castle Road, Edinburgh; William Alexander McCubbin, Mill Bank House, West Derby, Liverpool; William Stagg, 52, Seymour Road, Bristol.

Of the following papers, those marked * were read:—

*51. "Invertase: a Contribution to the History of an Enzyme or Unorganised Ferment." By C. O'SULLIVAN, F.R.S., and FRED. W. TOMPSON.

The substance present in yeast, &c., known as *invertase*, which possesses the power, under suitable conditions, of inducing the hydrolysis of cane-sugar, has been studied by the authors with the object of determining the precise manner in which it acts and its constitution.

The method adopted in determining the functions of invertase is essentially that developed by Vernon Harcourt in his paper "On the Observation of the Course of Chemical Change." A solution of cane-sugar was mixed with a measured amount of invertase, and the action was allowed to take place at a known temperature during a definite time; action was then stopped by the addition of alkali, and its extent determined.

The authors arrive at the following conclusions:—

1. The rate of hydrolysis of cane-sugar by means of invertase may always be expressed by a definite time-curve; this curve is practically that given by Harcourt as expressing a chemical change "of which no condition varies excepting the diminution of the changing substance." There are, however, some slight and apparently constant variations from the theoretical curve.

2. Whatever the conditions may be under which hydrolysis is taking place, as long as these conditions remain unchanged, this curve is adhered to.

3. When the degree of acidity is that most favourable for the action of invertase, the rapidity of the action is in proportion to the amount of invertase present.

4. The most favourable concentration of the sugar solution at a temperature of 54° C. is about 20 per cent. Below that there is a rapid decline in the speed of hydrolysis. Greater concentrations are only slightly less favourable until about 40 grms. per 100 c.c. is reached. In saturated solutions hydrolysis only proceeds with extreme slowness.

5. The speed of hydrolysis increases rapidly with the temperature until 55–60° C. is reached. At 65° C. the invertase is slowly destroyed, and at 75° C. it is immediately destroyed. At the lower temperatures the speed of the action increases with rise of temperature in accordance with Harcourt's law: the rate being about doubled for 10° rise; but above 30° C. the increase is not nearly so rapid.

6. Elevated temperatures have no permanent effect on the activity of the invertase so long as they are not sufficiently high to destroy it.

7. The caustic alkalis, even in very small proportions, are instantly and irretrievably destructive of invertase.

8. Minute quantities of sulphuric acid are exceedingly favourable to the action, but a slight increase of acidity beyond the most favourable point is very detrimental. The most favourable amount of acid increases to some extent with the proportion of invertase, and decreases with rise of temperature, but the authors have not been able to discover on what it depends.

9. In studying the action of invertase it is of the utmost importance that the most favourable amount of acid should be employed; otherwise, correct results cannot be obtained. At a temperature of 60° C. the action is almost stopped unless exactly the right amount of acid is used, whilst if this factor is properly adjusted hydrolysis proceeds at (probably) the maximum speed.

10. The influence of alcohol varies in direct proportion with the amount present. 5 per cent of alcohol decreases the speed of the action by about one-half.

11. The dextrose formed by the action of invertase is initially in the birotatory state.

12. The optical activity of a solution undergoing hydrolysis is no guide to the amount of hydrolysis that has taken place.

13. If a caustic alkali be added to a solution undergoing hydrolysis, and the optical activity be allowed sufficient time to become constant, it is a true indicator of the amount of inversion that had taken place at the moment of adding the alkali.

14. A sample of invertase which had induced hydrolysis of 100,000 times its own weight of cane-sugar was still active.

15. Invertase itself is not injured or destroyed during its action on cane-sugar.

16. There is no limit to the amount of sugar which can be hydrolysed with the aid of invertase.

17. The hydrolysis of cane-sugar by means of invertase is a simple chemical change differing in no important way from those which inorganic substances undergo.

18. The products of hydrolysis have no influence on the rate of the action.

19. A solution of invertase will withstand a temperature 25° C. higher in the presence of cane-sugar than in its absence.

20. The authors are of opinion that when invertase in-

verts cane-sugar combination takes place between the two substances, and that the invertase remains in combination with the invert sugar. This combination breaks up in the presence of molecules of cane-sugar.

21. A means of estimating the activity of a material containing invertase has been devised which consists in recording the result by means of the time factor $\pm 0 = x$ min. In this equation $\pm 0 =$ a certain definite amount of work, and $x =$ the time necessary to perform it. The expression means that the given inverting material takes x minutes to invert a standard amount of cane-sugar under standard conditions. The number x varies in inverse proportion to the actual amount of invertase contained in the material or materials under examination.

22. If sound brewers' yeast be pressed and then kept at the ordinary temperature for a month or two, it does not undergo putrefaction, but changes into a heavy yellow liquid; the product possesses no power of fermentation, but an apparent increase takes place in the invertive power.

23. From such liquefied yeast it is easy to filter off a bright solution of high hydrolytic power. It is shown that all the invertase of the yeast is in this solution, which is termed yeast liquor.

24. Yeast liquor has a relative density of about 1.080. It will remain for a long time unaltered, excepting that the colour darkens. If exposed to the air it may slowly become covered with mould.

25. If spirit be added to the yeast liquor until the mixture contains 47 per cent of alcohol, the whole of the invertase separates with only a slight loss of power. This precipitated invertase may be washed with spirit of the same strength and then the residue either dehydrated with strong alcohol and dried *in vacuo*, or else it may be extracted by means of 10 to 20 per cent alcohol and then filtered. The filtrate contains the invertase. On one occasion the extent of the loss involved by this process was determined, and it was found that all the invertase of the yeast liquor was present in the filtrate except 12.3 per cent.

26. The authors have not succeeded in further purifying invertase preparations carefully made in this manner. The slightest attempt at purification destroys the invertase.

27. They have prepared invertase almost free from ash.

28. The inverting power of pressed English yeast varies from $0 = 1000''$ to $\pm 0 = \pm 3000''$, or about $\frac{1}{3}$ of these amounts if calculated on the dry solid matter of the yeast.

29. The inverting power of the most active invertase preparation made was $\pm 0 = 25.1$ on the dry solid matter. It is believed that pure invertase would approximately have $\pm 0 = 22.5$ min.

30. The dry solid matter of yeast contains from 2 to 6 per cent of invertase. 5.8 per cent of invertase was separated from one sample of yeast.

31. During the preparation of invertase from yeast liquor an albumenoid is obtained, which is not redissolved by water. This is termed yeast albumenoid.

32. Invertase when it approaches a pure state is a very unstable substance. The products of its decomposition have been carefully examined and are found to constitute a new series of substances belonging to the *invertan series*.

33. The invertan series is a homologous series of substances which on analysis yield numbers which may be expressed in terms of an albumenoid and a carbohydrate. Seven members of the series are described.

34. The authors consider that invertase itself is a member of the invertan series and call it β -invertan.

35. If the products of the decomposition of β -invertan are examined, it is usually found that they consist of α - and δ -invertan. The former contains more, and the latter less, nitrogen than invertase.

36. α -Invertan is insoluble in water, and in all its other properties seems to resemble yeast albumenoid. It contains 8.35 per cent N. It is a very stable substance.

37. β -Invertan or invertase is soluble in water, and is the only member of the series which has the power of inverting cane-sugar. It contains about 3.69 per cent N, and its optical activity is $[\alpha]_D = +80^\circ$ (?).

38. γ - and δ -invertan are the products of the simplification of invertase. One or other of these two substances seems invariably to be formed. They both contain less nitrogen than invertase, and are always accompanied by α -invertan. Both are readily soluble in water. They contain respectively 3.15 and 2.43 per cent N, and their optical activity is $[\alpha]_D = +45^\circ$ and $+54^\circ$.

39. ϵ -Invertan is formed from the slow breaking down of δ -invertan. At the same time an insoluble substance, resembling α -invertan, is formed. This probably consists of another member of the series coming between α - and β -invertan. ϵ -Invertan is soluble in water, and has $[\alpha]_D = +65^\circ$. It contains 2.07 per cent N.

40. ζ -Invertan results from the splitting up of ϵ -invertan in the same way that the latter is formed from δ -invertan. Its optical activity is $[\alpha]_D = +75^\circ$, and it yields 1.61 per cent N.

41. η -Invertan is formed by the action of boiling sulphuric acid on ζ -invertan. It contains less nitrogen than the latter substance, but the substance has not yet been sufficiently investigated to give reliable figures.

42. The further products of the action of sulphuric acid on ζ -invertan are two soluble substances, one containing a considerable amount of nitrogen, and the other with little or no nitrogen, a high cupric reducing power, and a low (dextrorotatory) optical activity.

43. The properties of all the members of the series, except α -invertan, are very similar. They are all soluble in water forming bright solutions, which do not cloud on boiling. They are all readily thrown out of solution by alcohol, provided a little acid is present; the precipitates so formed are transparent colourless syrups, miscible with water in all proportions. The solutions are all dextrorotatory.

44. All the members of the invertan series, except η -invertan, yield a pink colouration on boiling with Millon's reagent.

45. All the members of the invertan series, except α -invertan, when submitted to the action of an alkaline copper solution, readily yield a very characteristic copper compound, from which the invertan (except β -invertan) may be separated unaltered. Invertan can probably form several such copper compounds, all having a similar appearance but affording different percentages of copper oxide.

46. In the presence of a very large excess of alkali, a copper compound is also formed from α -invertan, but on examination it is found that the α -invertan has been split up into an albumenoid and ζ -invertan, the copper compound being that of ζ -invertan.

47. It is believed that the members of the invertan series are combinations of yeast albumenoid with η -invertan, and that yeast albumenoid itself is probably a combination of yeast albumenoid with a carbohydrate.

48. According to this theory the composition of the carbohydrate present in the invertan series, calculated from the average of all the analyses, would be C = 43.22 per cent and H = 6.28 per cent. These numbers agree very closely with those required by a hypothetical carbohydrate coming midway between the *in* and the *on* groups.

49. It is thought that η -invertan contains 18 parts by weight of this carbohydrate to 1 of albumenoid, and that α -invertan contains 3 parts of the carbohydrate to 4 of albumenoid.

50. The other members of the series are formed by the union of these two substances according to the general formula $\eta + a\alpha$, where η represents η -invertan and α represents α -invertan. In this way we look upon invertase (β -invertan) as $\eta\alpha$. This splits up into α - and γ -invertan according to the formula $\eta\alpha = \eta\alpha_1 + \alpha$. $\eta\alpha_1$

represents γ -invertan, and this may be further transformed by elimination of α into $\eta\alpha$, or δ -invertan.

60. The numbers calculated for the constitution of the above theoretical homologous series agree with considerable closeness with those obtained from the analysis of members of the invertan series.

61. The number obtained from a single determination by Raoult's freezing process for the molecular weight of ζ -invertan is considerably less than the possible molecular weight of ζ -invertan, according to the authors' theory of its constitution.

*52. "The Action of Carbon Monoxide on Nickel." By LUDWIG MOND, C. LANGER, Ph.D., and F. QUINCKE, Ph.D.

When carbon monoxide is passed over finely divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400° , at a temperature between 350° and 450° , carbon dioxide is formed, and the nickel is gradually converted into a black amorphous powder, consisting of carbon and nickel; the composition of this deposit varies widely with temperature and time. A small quantity of nickel can thus change a very large amount of carbon monoxide, the action being complete and rapid at first, and continuing, although at a diminished rate for several weeks. A product containing as much as 85 parts carbon to 15 parts nickel has been obtained. Acids only partially remove the nickel; the carbon is very readily acted on by steam, carbon dioxide, and hydrogen without a trace of carbon monoxide being formed at a temperature of 350° .

On allowing the substance to cool in a current of carbon monoxide, it was noticed that the flame of a Bunsen burner into which the escaping gas was introduced became luminous, and when the tube through which the gas passed was heated, a deposit of nickel, mixed with a small quantity of carbon, was obtained. The authors were thus led to discover the existence of a volatile nickel compound.

To prepare this compound, a combustion tube is filled with nickel oxide, and this is reduced by hydrogen at about 400° ; after cooling the nickel to about 100° , pure dry carbon monoxide is passed over it without further heating, and the issuing gas is led through a tube placed in a freezing mixture: the major portion of the nickel compound condenses as a colourless liquid, but the gas retains about 5 per cent, and is therefore collected, dried, and again passed over the metal. When no more liquid condenses, the nickel is again heated to about 400° in a slow current of pure carbon monoxide; it is then cooled to about 100° , and again submitted to the action of the gas.

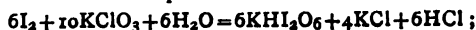
Nickel carbon oxide thus prepared is a colourless liquid which boils at 43° under 751 m.m. pressure; its relative density at 17° is 1.3185. It solidifies at -25° to a mass of needle shaped crystals. Its composition is represented by the formula $\text{Ni}(\text{CO})_4$. It dissolves in alcohol, and more readily in benzene and chloroform; dilute acids and alkalis have no action on it, but it is oxidised by concentrated nitric acid. It reduces an ammoniacal solution of cupric chloride, and it also causes the separation of silver from an ammoniacal solution of silver chloride. It interacts with chlorine, forming nickel chloride and carbon oxychloride. It is decomposed at 180° (in boiling aniline vapour) into nickel and carbon monoxide. The atomic weight of the deposited metal was found in three experiments to be 58.52—58.64, a result closely corresponding with Russell's value, 58.74.

Numerous experiments to obtain similar compounds with other metals, notably with cobalt, iron, copper, and platinum, led to negative results. On experimenting with specially purified cobalt, in the beginning a slight coloration of the Bunsen flame into which the gas was led was noticed, but after a time this was no longer observed. Commercial cobalt afforded a gas which deposited a mirror of pure nickel, it being possible, in fact, to purify cobalt from nickel by carbonic oxide. The nickel mirrors

obtained by heating the carbonic oxide compound do not appear to contain any trace of cobalt.

*53. "The Interaction of Iodine, Water, and Potassium Chlorate." By HENRY BASSETT.

The author finds that the usual statement that the chlorine in potassium chlorate is directly displaced by iodine when subjected to treatment in accordance with Millon's directions is incorrect; he considers that the evolution of chlorine observed by Millon is due to a secondary interaction, $\text{HIO}_3 + 5\text{HCl} = 3\text{H}_2\text{O} + \text{ICl} + 2\text{Cl}_2$, which takes place when the iodine is added all at once, and is due doubtless to the rapid formation of iodic acid and hydrogen chloride within the dense mass of iodine. His experiments show that the iodate is formed in accordance with the equation—



and that on evaporating the solution to dryness on the water-bath, decomposition of a portion of the biniodate takes place:—



*54. "The Milk of the Gamoose." By A. PAPPEL and H. D. RICHMOND, Khedival Laboratory, Cairo.

The milk of the Egyptian gamoose or buffalo (*Bos Bubalus*) is distinguished from that of the cow by its white colour and peculiar musk-like smell. The authors find the average composition to be as follows:—

Water	84.10		
Fat	5.56		
Sugar	5.41		
Casein	3.26	containing N	0.511
Albumen	0.60	"	0.094
Nitrogen bases ..	0.09	"	0.035
Salts	1.03		

The fat was found to vary from 7.35 to 5.15 per cent, and the solids not fat from 10.67 to 10.07 per cent. The average relative density at 15.5° was 1.0354; the increase in eight hours after milking was 0.0006, and in twenty-four hours 0.0007. Gamoose milk, therefore, differs from that of the cow, both in the high percentage of fat and of solids not fat, the increase in the latter being largely due to the sugar.

Comparing the fat with that of cows' milk, the chief differences noted by the authors are, (1) the presence of small quantities of sulphur and phosphorus; (2) the presence of fatty acids soluble in boiling water, but not volatile in much larger amount than in cows' milk; (3) the presence of fatty acids giving lead salts soluble in ether but not members of the oleic series; (4) the difference in the ratio between caproic and butyric acid—4:1 instead of 2:1. Other alcohols than glycerol do not appear to be present.

The sugar appears not only to be different from milk sugar, but novel, its rotatory power being $[\alpha]_D = 48.7$, and its cupric-reducing power $\kappa = 73.7$; it yields only dextrose on hydrolysis. It is proposed to name it *temphose*.

The authors also state that the milk contains a small amount of citric acid.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 5, August 4, 1890.

The Exhaustion of Soils by Cultivation without Manures. Second Memoir: Study of Drainage Water.—P. P. Dohérain.—The author has studied the cultivation of the experimental fields of Grignon, which

have been kept without manure since 1875. The fields still yield good crops of oats; the yield of wheat is tolerable, but the cultivation of beets and of clover has become impossible. On proceeding to a comparative analysis of the exhausted soils and of some neighbouring soils which have been well manured he found that the respective quantities of nitrogen, phosphoric acid, and potassa differed very little, but the carbon in the organic matter varied from a single to a double proportion; in the unmanured lands there were only 7 grms. of organic carbon per kilo. of soil as against 15 to 16 grms. in the manured soils. Hence he resolved to ascertain whether (1) the decrease of the organic matter occasioned their more rapid desiccation, i.e., a less aptitude to retain moisture, and (2) whether the organic matter of the exhausted soils had lost the power of producing nitrates. In the experiments carried on from November, 1888, to November, 1889, the author found that the differences in humidity were very slight. He now examines the second question: if the organic matter of the exhausted soils was capable or incapable of producing a sufficient quantity of nitrates for the demands of good crop. He now finds, by gauging and analysing the drainage waters respectively from the manured and the unmanured lands, that in their aptitude for the production of nitrates there is no difference sufficient to explain why the one soil is fertile and the other barren.

The Density of Nitrogen and Oxygen according to Regnault, and the Composition of Air according to Dumas and Boussingault.—A. Leduc.—The author finds a discrepancy between the results of Regnault and the composition of the atmosphere as given by Dumas and Boussingault, which he thinks can be accounted for only by an error on the part of Regnault.

Reactions of the Salts of the Alkaloids.—Albert Colson.—In studying the action of bases upon dissolved salts, the author finds some endothermic reactions both within and outside of liquids at low and sensibly constant temperatures. In these reactions the laws of Berthollet seem to predominate over the thermic laws. For bases of the same order the laws of Berthollet are applicable, whatever is the direction of the heats liberated.

Division of Hydrogen Sulphide between the Metals of Two Dissolved Salts.—G. Chesneau.—The author's experiments show that in the incomplete precipitation of copper and lead nitrates dissolved in equal equivalents by hydrogen sulphide, the division of the hydrogen sulphide between the two metals takes place in the direction indicated by the formation-heats of the sulphides, and varies progressively with the quantity of H_2S . The proportion of the copper to the lead precipitated by H_2S varies with the time; it decreases at first, reaches a minimum after a few minutes, and then slowly increases.

Some Derivatives of Acetyl-acetone.—A. Combes.—The author has obtained and studied the cupric derivative of monochloroacetylacetone.

Combinations of Hæmoglobine with Carbonic Acid and with a Mixture of Carbonic Acid and Oxygen.—Christian Bohr.—The following combinations of hæmoglobine and carbonic acid have been observed:—(1) a hæmoglobine which, at a pressure of $CO_2 = 60$ m.m. at a temperature of 18° fixes about 3 c.c. of CO_2 . This the author designates carbohæmoglobine γ ; (2) a hæmoglobine which, at the same pressure and the same temperature, fixes about 6 c.c. of CO_2 (carbohæmoglobine δ); (3) a hæmoglobine observed by Jobin which, under the same conditions, fixes 1.5 c.c. CO_2 (carbohæmoglobine β). If a solution of hæmoglobine is shaken up with a mixture of oxygen and carbonic acid, the hæmoglobine absorbs both, forming with them an unstable compound, and this as if each gas were alone. As the carbonic acid and the oxygen are absorbed independently of each other, we may admit that they are fixed by different parts of the hæmoglobine.

Colouration of Silk by the Food of the Silkworm.—Louis Blanc.—Only some very soluble and very diffusible dyes, such as magenta, are capable of being absorbed by the intestinal epithelium of the silkworm; such substances may then colour the cellulose of the organs which secrete silk, but they do not colour the product secreted. The coloured silks which have been obtained by submitting silkworms to some special diet are very probably merely charged externally with coloured dust.

Société Nationale d'Encouragement pour l'Industrie.
Session of July 25, 1890.

M. de Luynes presented, on behalf of M. Reimer, specimens of synthetic phenic acid prepared at Neuville-sur-Saône at the branch works of the Baden Aniline Company. This acid is quite colourless; it melts at 41° , boils at 178° , and yields limpid solutions. Its slight odour differs from that of the purest phenols of commerce. On account of its properties and its low price it is likely to supersede ordinary phenol in its applications to medicine, to the preservation of putrescible articles, and in the manufacture of chemical products.

M. Le Chatelier made a communication on the measurement of high temperatures developed in furnaces. The indications of Wedgwood are not comparable among themselves; the air-thermometer has to be rejected on account of its fragility and its complicated nature. Very commonly industrialists judge of temperatures by the colour of the radiations emitted. This process may be improved by the use of a cobalt glass, or better, of an optical system consisting of quartz between two Nicols, which renders it possible to arrest at will one of the mean radiations of the spectrum. The most exact of the pyrometers proposed is the thermo-electric apparatus devised in 1832 by Becquerel, and now rendered practicable by the removal of certain difficulties of detail.

M. Lion presented a photometric balance, depending on the destructive action which light exerts on nitrogen iodide. If obtained by allowing ammonia at 25° to act upon iodine, this substance may be managed without the slightest danger if it is kept in the liquid, and it yields a supply of nitrogen which varies with the intensity of the illumination. The liberation of nitrogen begins and ceases instantly with the luminous impression.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 54.

Raffinose.—L. Lindet.—It is disputed whether raffinose pre-exists in beets or if it is formed under the influence of weak alkalies. According to MM. Tollens and Richbeil it is identical with the gossypose from cotton-seed. It cannot be confounded, as Schiebler and Tollens pretend, with Berthelot's melitose. This substance can be split up into raffinose and eucalyne. Its taste is but slightly sweet. Its composition is $C_{36}H_{52}O_{21}$.

THE MASON COLLEGE, BIRMINGHAM.

SESSION 1890-gr.

Faculties of Arts and Science.

The next SESSION commences on Tuesday, September, 30, 1890. A SYLLABUS containing full information as to the various Courses of Instruction, Lecture Days and hours, Fees, Scholarships, &c., is published by Messrs. Cornish, New Street, Birmingham, price 6d., post free, 6d.

Further particulars may be obtained on application to the Secretary, at the College.

R. S. HEATH, Principal.
GEO. H. MORLEY, Secretary.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1605.

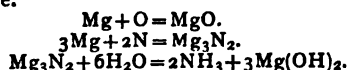
AMMONIA FORMED BY BURNING METALLIC MAGNESIUM IN CONTACT WITH ATMOSPHERIC AIR.

By P. L. ASLANOGLU.

We all know that by burning metallic magnesium in contact with atmospheric air it burns with a bright white light rich in chemically active rays, forming magnesium oxide (MgO), the only oxide as yet known, which is liberated from the metallic magnesium as a fine white powder. But there is still a portion of burnt magnesium remaining in the dish, and this is magnesium hydrate—Mg(OH)₂.

In November last (1889) I was experimenting with magnesium. I was burning an ounce of magnesium dust (superior quality) in an iron dish by setting fire directly to the powder; it burnt as usual, and on cooling I examined what remained and found that a strong smell of ammonia proceeded from the remaining powder, magnesium hydrate; I have repeated the same experiment several times with all the different qualities or specimens of magnesium dust I could get, and they all gave the same result; I have also burnt magnesium wire, which likewise gave the same result.

From results obtained I have concluded that magnesium burns in contact with the oxygen of the air, forming magnesium oxide; and that it also burns with the nitrogen and forms ammonia and magnesium hydrate, absorbing at the same time the aqueous vapour of the atmosphere.

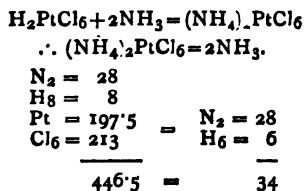


It is evident, therefore, that the quantitative amount of nitrogen and aqueous vapour contained in this magnesium hydrate will vary with the different atmosphere found in different towns, countries, districts, &c.

I should think that by this experiment we could estimate the composition of the atmosphere, as its constituents are present in this magnesium mixture.

I have not yet made the quantitative analysis of the above experiment for the estimation of nitrogen, but the best way of estimating it would seem to be the following:—

By passing steam through the powder to collect the ammonia hydrate and receive it in a well-closed flask, then to precipitate it with platinum chloride, and estimate the ammonium platino-chloride precipitated. This will be sufficient to estimate the ammonia, and consequently also the nitrogen present, thus:—



Suppose, for instance, we get by analysis 45 grms. of ammonium platino-chloride; then the amount of NH₃ contained will be—

$$446.5 : 34 :: 45 : x.$$

Six months after this experiment I was informed by an eminent authority on the science, to whom

I imparted my observations, that this phenomenon had been previously observed by an American. Consequently I have hitherto doubted whether to insert it in the CHEMICAL NEWS or not; but, however, on second thoughts I decided to send the above to the editor of the CHEMICAL NEWS, asking him to judge of my work and to publish it or not, as he thinks advisable.

I myself have not yet seen a notice of the experiment in question in any English chemical paper, but I may have missed it, and thus have been anticipated in this record without my knowledge.

University College, London,
Gower Street, W.C.

A SUMMARY OF FOOD ANALYSES, SHOWING THE MORE IMPORTANT ADULTERATIONS THAT MAY BE SUSPECTED TO BE PRESENT.

By H. N. WARREN, Research Analyst.

THE accompanying details, which comprise examination of some of our more important articles of consumption, are intended not so much to enter into the more lengthy or direct means of analysis, but to state as briefly as possible the numerous adulterants that have from time to time been met with by myself.

In the first instance I would mention a few of the worst cases of adulteration that are to be met with in the manufacture of sweetmeats. A compound known by the name of chewing gum has for years been sold by confectioners, which consists of about 80 per cent of paraffin, a small quantity of sugar, and various flavouring matters. As regards the composition of lozenges, inorganic elements play a considerable part; for out of an average of twelve samples, ten contained nothing but a trace of saccharine, the remaining ingredients comprising chalk and silica. Several samples of cheap Spanish liquorice contained 25 per cent of clay, and two samples entirely placed these out of sunlight by being composed of raw sugar and ground coke. Chocolate contains frequently quantities of sand, fuller's earth, and iron ore; as a colouring agent chromic acid is frequently resorted to, and introduced in the form of potassium chromate, whereas a fine blue is also frequently imitated by means of cupric sulphate, and that of nickel sulphate when green is desired; and lastly, but by no means least injurious, may be mentioned the practice of coating sweets with metallic tin, not as a wrapper only, but to create a metallic surface in several instances. I have met with samples of this description where of every half-dozen sweets that were consumed upwards of two grains of metallic tin would thus be introduced into the system.

(To be continued).

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RECOVERY OF ABSORBED MORPHINE FROM THE URINE, THE BLOOD, AND THE TISSUES.*

By THEODORE G. WORMLEY, M.D., LL.D.,
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University of Pennsylvania.

(Concluded from p. 81).

CASE IV.—Administered subcutaneously to a dog weighing 14 kilos. 0.1 grm. morphine, dissolved as acetate in 10 c.c. water. Symptoms of the poison soon appeared.

a. Two hours after the injection obtained 14 c.c. very turbid, strongly alkaline urine. The final residue from

* From the *University Medical Magazine*.

this urine readily indicated, under the action of several tests, the presence of morphine in quite decided quantity.

b. Sixteen c.c. urine withdrawn at the end of four and a half hours also showed the presence of the alkaloid in diminished quantity.

c. Fifty-five c.c. urine withdrawn at the end of twenty-eight hours distinctly indicated the presence of morphine in very minute quantity.

CASE V.—A man habituated to the use of morphine in large quantity took daily for some time six grains (0.389 gm.) morphine sulphate. While taking this quantity the urine passed December 28, 1889, during twenty-four hours measured 440 c.c., was about neutral in reaction, and of sp. gr. 1012. For this case I am indebted to my colleague, Professor H. C. Wood.

Two hundred and twenty c.c. of the urine, acidulated with acetic acid, were concentrated to 75 c.c., rendered alkaline by ammonia, and extracted with about two volumes hot amyl alcohol. The residue obtained on the evaporation of the alcohol readily showed the presence of morphine. After further purification the residue, under the action of several tests, indicated the presence of morphine in very marked quantity, the reactions being about as well-marked as with the pure alkaloid, but repeated attempts failed to obtain it in the form of well-defined crystals.

CASE VI.—A man affected with polyuria, accustomed for some years to the use of large quantities of crude opium, was, at the time of this examination, taking daily 60 grains (3.9 grms.) of the drug in 20-grain doses three times a day.

The urine voided during twenty-four hours, January 4, 1890, measured 4040 c.c., had a distinctly alkaline reaction, and sp. gr. 1007.

One thousand c.c. of the urine reduced to 100 c.c. and extracted with amyl alcohol in the usual manner furnished, under the various tests, very satisfactory evidence of the presence of morphine in quite notable quantity.

An attempt was made to also ascertain the presence of meconic acid, but on account of the presence of the phosphates and other interfering substances the results were not satisfactory.

CASE VII.—Dr. W. H. Price, of the University Hospital, kindly furnished me the following case:—A coachman, aged 50, greatly depressed in spirits, swallowed, February 13, 1890, a fluid ounce of ordinary laudanum. When seen by Dr. J. Daland, thirty-five minutes afterwards, the patient was in a comatose state; the pupils were contracted to a point, and the respirations four per minute.

Under the use of strychnine and atropine hypodermically, electricity, and other active measures, at the end of thirty hours the patient was quite himself again.

Eight hours after the poison had been taken about 250 c.c. urine was withdrawn from the bladder by catheterisation; 160 c.c. of this urine, reduced to 75 c.c., was extracted by amyl alcohol; and this extract purified by a second, and then a third, extraction by the alcohol, and finally by ether.

The final residue, when examined by Frøehde, Husemann's, the nitric acid, and iron tests, very clearly showed the presence of morphine. The urine in this case was not examined until the third day after its withdrawal.

CASE VIII.—A man with suicidal intent, took at 10 p.m., March 10, 1890, ten fluid drachms of laudanum. When seen ten hours thereafter by Dr. J. Daland, who kindly furnished me the particulars of the case, the patient was in a state of great stupor, from which he could be partially aroused. Under moderate treatment he soon recovered. The first urine voided by the patient was lost.

About twenty hours after the poison had been taken 120 c.c. of very turbid urine, of slightly acid reaction and sp. gr. 1022, was collected. This, after addition of acetic

acid, was filtered, then reduced to 50 c.c., and extracted in the usual manner by hot amyl alcohol.

The residue obtained on evaporating the alcohol was extracted by ether, and this liquid allowed to evaporate spontaneously. The ether residue very clearly showed the presence of morphine, but only in very minute quantity.

It should be added that the only evidence that ten drachms of laudanum had been taken in this case is the statement of the patient himself; nor is anything known in regard to the quality of the drug taken.

CASE IX.—A gentleman on retiring at night took, by way of experiment, a pellet containing $\frac{1}{2}$ grain (16 m.g.) morphine sulphate. The following morning he voided 185 c.c. urine of light colour and slightly acid reaction.

This, after concentration, was extracted by amyl alcohol in the usual manner. The residue from this alcohol was again extracted by the alcohol, and the operation repeated a third time with a fresh portion of the alcohol.

The residue from the third alcohol extract, when examined by Frøehde's reagent, promptly gave a colouration very similar at least to that of morphine, but the results were not fully satisfactory. Other portions of the residue very promptly reduced solutions of iodic acid and of potassium ferricyanide; but, under the conditions, these reactions have no positive value.

A urine extract of this kind, even in the absence of morphine, will frequently yield, with Frøehde's reagent, a colouration which might be mistaken for that of a minute quantity of morphine, due to the reduction of the molybdenum compound. Moreover, this reducing action may entirely prevent or mask the normal reaction of morphine, even when the alkaloid is added to the residue in very notable quantity, as we have seen in repeated experiments.

For the purification of a mixture or residue of this kind it may be treated with a little water and a drop of acetic acid. The liquid is then filtered, and, while still acid, extracted with several volumes of pure strong ether.

The ether being decanted, the aqueous liquid is again covered with several volumes of fresh ether, and a drop of ammonia, or sufficient to neutralise the acid added. The mixture is then quickly and thoroughly agitated. The ether will now take up any morphine present, in part at least, and at most only a trace of urea, if present, the extractive matters and greater portion of urea being retained by the aqueous fluid. The ether is then decanted and allowed to evaporate spontaneously. Since morphine is only very sparingly soluble in ether, this method of purification is applicable only for the recovery of minute quantities of the alkaloid.

The above residue, from the third amyl alcohol extract, when extracted by ether after the foregoing method, gave a very minute, about colourless residue, which, when examined in several portions by Frøehde's reagent, gave purple colourations which seemed to leave no doubt of the presence of morphine.

CASE X.—This was a repetition of the foregoing case, only that $\frac{1}{2}$ grain morphine sulphate was taken, and the next morning 350 c.c. of urine, of faintly acid reaction and sp. gr. 1012, was obtained.

After concentration the urine was extracted by amyl alcohol and finally by ether, in the same manner as in the previous case.

The very minute final ether residue, when examined in three or four portions by Frøehde's reagent, gave well-marked purplish or violet colourations. These results were quite in contrast with those obtained by the reagent from an exceedingly minute residue obtained in the same manner from urine known to be free from morphine.

General Considerations.

In the use of amyl alcohol for the extraction of morphine from the urine, the urea taken up with the morphine interferes more or less with the purification of the alkaloid. In a residue consisting of a mixture of this kind,

the urea, as such, may, as we have found, be decomposed by heating the mixture in an air oven for a few hours at 135° C., without any appreciable loss of the morphine. But the presence of the products of the decomposition of the urea prove about as objectionable as that of the urea itself. Since urea is freely soluble in water, whilst morphine is only sparingly soluble, it might be inferred that these substances could thus be readily separated. This is true in regard to pure mixtures, and also when the morphine has assumed the crystalline state; but when present in only minute quantity the alkaloid seems to be so closely adherent with the urea and colouring-matter that these substances are largely dissolved together.

Some experiments were made in regard to the adaptability of *isobutyl alcohol* for the extraction of morphine from complex mixtures, especially from the urine. For this purpose, Schuchardt's alcohol, apparently pure, was employed. If a small quantity of this alcohol be agitated with large excess of water, it is dissolved by the water in the proportion of one volume of the alcohol in about 10.5 volumes of water, as generally stated by writers.

If, however, equal volumes of the alcohol and water, say 100 volumes of each, be mixed and agitated, after repose the alcoholic liquid will measure 103 volumes, the aqueous fluid being reduced to 97 volumes—that is, 100 volumes of the alcohol will take up 3 volumes of water. On treating excess of finely powdered morphine with hot *isobutyl alcohol*, and allowing the mixture to stand sixteen hours, it was found that one part of morphine was held in solution by 110 parts by weight of the alcohol. Under the same conditions one part of urea was retained in solution by 49.8 parts by weight of the alcohol.

It would thus appear that morphine, while rather freely soluble in *isobutyl alcohol*, is slightly less soluble in this liquid than in *amyl alcohol*; whereas urea, on the other hand, is somewhat more freely soluble in *isobutyl alcohol* than in *amyl alcohol*.

THE FIXATION OF ATMOSPHERIC NITROGEN.*

By A. A. BRENNEMAN, S.B.†
(Continued from p. 95.)

Production of Cyanides from Ammonia.

THE reactions by which ammonia is converted into cyanides are so closely related to the direct production of cyanides from nitrogen, and offer so many points of suggestion in connection with the same, regarded as an industrial problem, that the history of them cannot be omitted from this summary.

The original experiment, ascribed by Langlois (*Ann. ch. phys.*, [3] i., 117) to Scheele, of heating together sal-ammoniac, potash, and charcoal and obtaining potassium cyanide, may be regarded as the starting point.

Liebig attributes to Scheele (1750—80?) the statement, that ammonia passed over hot charcoal yields hydrocyanic acid, but Langlois does not find this in Scheele's writings. What Scheele does say is that when sal-ammoniac is heated with vegetable charcoal and potash the mass yielded on lixivation "*la lessive du sang*."‡ (*Langlois, loc. cit.*)

* *Journal of the American Chemical Society*, vol. xi., Nos. 1—2.

† The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

‡ That is, potassium ferrocyanide, yellow prussiate of potash, called also in German "*blutlaugensalz*." The iron must have come from impurities in the materials. In the "*Life of Scheele*," given in *Crell's Journal*, vol. i., p. 12, 1897, the author says: "His experiments on the colouring matter of prussian blue, the methods of separating it, its properties, and in short the discovery of its artificial composition from charcoal, fixed alkali, and sal-ammoniac, may be mentioned amongst the most valuable of the performances with which he has presented us." The biographer also refers to fuller accounts of this work in *The New Transactions of the Royal Stockholm Academy*, vol. iii., p. 256, and vol. iv., p. 32. These sources of information are not accessible to me.—B.

Clouet in 1791* mentioned that ammonia gas passed over hot charcoal yields hydrocyanic acid. He states that Thenard had noticed that a soluble substance having the odour of bitter almonds was formed under the same conditions. Bonjour, Vauquelin, Buchholz, Schroder, and Ittner (*J. pr. Ch.*, xxvi., 409) all refer to the same fact as based upon experiments in which ammonia or ammonium chloride was heated with charcoal or with mixtures of charcoal and lime or oxide of lead. The product was probably ammonium cyanide, as in later repetitions of similar experiments, but the constitution of the cyanides was not then understood, as this was before the date of Gay-Lussac's discovery (1814). Clouet reported that hydrocarbons, carbonic acid, and nitrogen were set free at the same time, while Bonjour showed that hydrogen was the only by-product, an observation that was fully confirmed by Langlois in 1841. Trommsdorff (*Ibid.*) however, was first to recognise ammonium cyanide in the products of this experiment.

Kuhlmann (*Ibid.*, *Ann. Chem. (Liebig)*, xxxviii., 62; *J. pr. Ch.*, xvi., 482) found that volatile nitrogen compounds containing all hydrogen or mixed with volatile hydrocarbons, when passed together with carbonic oxide over hot platinum sponge, yielded ammonia. He refers to Clouet's experiment, and shows, by a repetition of the same, that no hydrocyanic acid, but only ammonium cyanide, is produced. Marsh-gas (CH_4) is separated at the same time. He regards the process of preparing alkaline cyanides as involving first the formation of ammonia, which, in presence of alkali and excess of carbon, is converted into cyanogen and carbonic oxide. Langlois (*Ann. ch. phys.*, [3], i., 117) repeated Scheele's experiment with sal-ammoniac, but obtained no cyanide. He also obtained ammonium cyanide by passing ammonia over hot charcoal, and called attention to the remarkable way in which ammonium cyanide resists decomposition at high temperatures.

The processes of Jacquemyn and Berry in this direction have already been mentioned (*ante*).

Graeger (*Jsb. chem. Tech.*, 1853, 184) passed vapour of ammonium carbonate through alkaline charcoal contained in narrow iron cylinders 1½ inches in diameter, and obtained 93 to 95 per cent of the theoretical yield of ferrocyanide. When large and wide cylinders were used the results were much inferior, only 15 to 30 per cent being obtained.

Brunquill (*Preuss. Verhandlungen*, 1856, 30; *Jsb. chem. Tech.*, 1856, 102; *Dingl. pol. J.*, cxl., 374, 452), in 1856, proposed to apply the same principle to the production of cyanides and prussiates. Ammonia, or the vapours from distillation of bones, &c., are passed over hot firebrick and then over hot wood charcoal in pieces of the size of a chestnut. The volatile ammonium cyanide is absorbed by solution of ferrous sulphate in an apparatus of peculiar construction. A portion of the ammonia is recovered as sulphate, and used anew in the process. The precipitated cyanides of iron are converted by potash or soda into prussiates. The advantages of this method are the prevention of waste of potash and of nitrogen. Only moderate temperatures being employed, there is no loss of potash by volatilisation, by absorption, or by formation of unavailable salts of potash, all of which occur in the old process. The cost of the ammonia is defrayed by the increased value of the residue when bones are used. The author hoped also to obtain ammonia for the first stage of the process by passing air and steam over coal.

Levoir, in 1859 (*J. pr. Ch.*, lxxvi., 447; *Dingl. pol. J.*, cliii., 466), noticed that a flame of ammoniacal gas yielded cyanogen (ammonium cyanide) in burning. Fischer (*Dingl. pol. J.*, clvii., 466) questioned this statement, saying that he had repeated Levoir's experiment with an

* *Ann. ch. phys.*, xi., 30; *J. pr. Ch.*, xxvi., 408. *Crell's Annalen*, 1796. This latter reference, which is probably the original source, I have not had access to.—B.

argand burner, and obtained no cyanogen. The fact was verified, however, a few years later by Romily.

H. Johnson (*Dingl. pol. J.*, clvi., 212; *Jsb. chem. Tech.*, 1860, 221, with diagram), in 1860, obtained in England a patent for a method, devised by J. V. Lucas in Paris, for preparation of prussiates, which consists simply in saturating wood charcoal with potash solution, drying and heating it to redness in a retort, and passing ammonia over it. The charcoal is mixed also with 5 per cent of iron filings.

J. Webster, in 1860 (Eng. Pat., No. 1913, Aug. 8, 1860), patented in England a process for manufacture of prussiates by charring or burning a mixture of sawdust or spent bark and oxide of iron, charging the mixture with potash and passing ammonia through it.

Fleck (*Polyt. Centralbl.*, 1863, 717; *Dingl. pol. J.*, clxix., 209; *Jsb. chem. Tech.*, 1863, 323), in 1863, proposed to make cyanides as follows:—A hot mixture of charcoal or coal, sulphur, and potash is treated with a definite quantity of ammonium sulphate. Potassium sulphocyanate is formed. Ammonia in part escapes, but is absorbed and utilised. The sulphocyanate is decomposed by metallic iron, yielding potassium cyanide and ferrous sulphide. It was claimed by the author that 94.42 per cent of the ammonium salts used were ultimately converted into cyanides. This process is referred to by Meyer ten years later, 1874, as not being successful in practice.

Gelis (*Annales du Conservatoire des Arts Metiers*, 1862, 37; *Jsb. chem. Tech.*, 1862, 283), in 1862, manufactured prussiates in Paris after a new method of his own invention, for which a medal was awarded at the London Exhibition of 1862. It consists in mixing, in the cold, a solution of ammonium sulphate (NH_4HS), obtained from gas liquor, with carbon disulphide; ammonium sulpho-carbonate, $(\text{NH}_4)_2\text{SCS}_2$, is formed and sulphuretted hydrogen. The addition of potassium sulphide to the sulphocarbonate results in the production of potassium sulphocyanate, which by action of iron can be converted into cyanide or prussiate. The by-products, ammonium sulphate and sulphuretted hydrogen, are again used. The process is carried on in a retort, and these products are readily recovered. The cost by this process was said by Payen to be within 1.6 francs per kilo. (about 15 cents per pound) for potassium ferrocyanide.

Meyer, in 1874 (*ante*), remarks that the conversion of potassium sulphocyanate into cyanide by iron is wasteful of nitrogen when fusion is resorted to and incomplete in the cold. The process of Gelis was finally abandoned.

Romily (*Compt. Rend.*, lxi., 320; lxi., 865; *Jsb. chem. Tech.*, 1867, 761), in 1867, repeated the experiment of Levoir (*ante*), and improved upon it. Illuminating gas was made to bubble through ammonia and then burned from a jet, and the flame was made to impinge upon a surface of water containing caustic potash in solution. Potassium cyanide was found after a time in the solution. Solutions of sodium and calcium hydrates gave corresponding results. When distilled water was used ammonium cyanide was found in the liquid. The effect was produced only when the flame was luminous or smoky; the flame of a Bunsen lamp yielded no cyanides. Vapours of oils or hydrocarbon gases containing ammonia gave similar results. Vapour of water in the mixture of gases did not prevent the formation of cyanides. When iron in fine powder was suspended in the alkaline solution ferrocyanide was formed.*

An apparatus was devised to apply the principle industrially. A cylinder of iron revolving on a horizontal axis, dipped into a tank containing an alkaline solution. A pipe, parallel with the cylinder and pierced with holes,

supplied ammoniacal illuminating gas, burning in a line of jets which impinged upon the face of the cylinder. The cyanides were absorbed by the film of alkaline liquid, which was continually renewed as the cylinder revolved.

Schwarz (*Bull. Soc. Chim.*, 1869, 167; *Dingl. pol. J.*, cxc., 399; *Jsb. chem. Tech.*, 1869, 269), in 1869, obtained ammonium cyanide by passing vapour of carbon disulphide mixed with ammonia over hot iron or copper in an iron tube. Sulphide of the metal is simultaneously formed. The vapours are passed into a mixture of solutions of caustic potash, ferrous sulphate, and ferric chloride, and the resulting mass is converted into prussian blue by hydrochloric acid, and then by potash into yellow prussiate. Schwarz also confirmed the conclusions of Levoir and Romily (*ante*) as to the production of ammonium cyanide during the combustion of ammoniacal illuminating gas, and he suggests that the purification of such gas from ammonia is, on this account, a matter of the greatest importance.

Frohde remarks ("Watt's Dict. Supp." I., 537) that the fumes from burning coal may be noxious, not merely because of oxides of carbon in them, but also because of cyanogen. He claims to have detected cyanogen by its odour where coal was incompletely burned.

E. Meyer (*Jsb. chem. Tech.*, 1874, 442), in 1874, published a review of the cyanogen industry up to the year of the Vienna Exhibition (1873). He found the old method still the only important one. The problem of making cyanides from nitrogen of the air was still unsolved, and the earlier efforts of Possoz and Boissiere (*ante*) had not been even equalled in its results by the later one of Margueritte and Sourdeval, from which much was at first expected. The methods using ammonia as a source of nitrogen for the manufacture of cyanides had not replaced the old method, through dry distillation of animal matters (Karmrodt, and others)—which are treated by fusion in the old process—nor by substitution of ammonia salts as a source of nitrogen for these substances (Fleck, *ante*). Neither had the methods based upon formation of sulphocyanate (Gelís) marked any great success. The production of sulphocyanate is readily brought about by Gelís's method, and the process is, so far, a success; but the conversion of this salt into cyanide or ferrocyanide is difficult. It does not stand sufficiently above the usual raw materials (animal matters) used for this purpose, in its proportion of nitrogen, to counterbalance the disadvantage which it offers in comparison with them from its high proportion of sulphur.

F. Maxwell-Lyte (U.S. Pat. 161, 137, March 23, 1875) patented, in 1875, a process for manufacture of ammonia by bringing nitrogen in contact with nascent hydrogen liberated in the presence of a triad or pentad element.

Tscherniak and Gunsberg (*Ber.*, 1879, 140; *Dingl. pol. J.*, ccxxii., 80; *Jsb. chem. Tech.*, 1879, 471; 1882, 570), in 1878, patented a method, in Germany (D. R. Pat. 3,199, April 9, 1878), for the manufacture of cyanides similar in principle to that of Schwarz (*ante*). Two parts of ammonia water of 85 per cent and one of carbon disulphide are put into a tight vessel, heated to 110° C. below and cooled above, so that a continuous distillation of the volatile substances occurs. After three or four hours the mixture is found to be converted into ammonium sulphocyanate and sulphuretted hydrogen. The ammonium salt is converted into calcium sulphocyanate, which, by action of an alkaline sulphate or carbonate, yields the corresponding alkaline salt, and this, by heating with coal, lime, and iron, yields cyanides or prussiates. The ammonia is recovered and used again.

Graham Young, in a process for the manufacture of ammonia patented in England in 1880, has suggested the use of electricity to effect the union of nitrogen and hydrogen. The principle had also been mentioned in an English patent issued to Chisholm and Kent in 1860. No practical result has as yet come from these suggestions.

* The discoveries of Levoir and Romily recall the early observations of Kuhlmann, who showed that ammonia and all volatile compounds of nitrogen yielded ammonium cyanide when mixed with hydrocarbons (or even with carbonic oxide in the case of ammonia), and passed over platinum sponge, at a temperature of 600° F.—B.

The Decomposition of Alkaline Hydrates by Metals in Presence of Air to Produce Ammonia.

Dufrené (Eng. Pat. No. 5478, Dec. 29th, 1880), in 1880, patented a process in England for the manufacture of ammonia by combustion of zinc in air, in presence of an alkaline hydrate. Hydrogen and nitrogen are both set free and combine to form ammonia under the influence of a porous solid, such as iron or platinum sponge in a heated state.

Twinch (Eng. Pat. No. 3712, Aug. 25th, 1881), in 1881, proposed to manufacture ammonia by using oxide of nitrogen (nitric oxide?—B.) to remove oxygen from air; the resulting nitrogen (which is said to be nascent and peculiarly active?—B.) is brought in contact with nascent hydrogen from the decomposition of steam or of alkaline hydrates by metals, to produce ammonia.

(To be continued).

THE DRY ASSAY OF TIN ORES.*

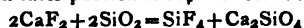
PART I.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Continued from p. 94).

2. *Fusion with Calcium Fluoride.*—There are three methods described under this head, in all of which fluor-spar is used as the only or principal flux. They are recommended for ores containing silica only.

Fluor-spar is not readily fusible; in fact, it cannot be melted at temperatures produced in a muffle-furnace. Assays requiring it as a flux must therefore be carried on in a pot-furnace. While difficult of fusion, it is liquid when melted, and assists to liquefy compounds which have a refractory character by holding in suspension the particles which cannot be completely melted. It is therefore very satisfactory if a high temperature is required. Berthier† was the first to suggest that a loss in weight takes place if calcium fluoride and silica are heated together. In later publications‡ the formula—



is found with the statement that part of the silica escaped as silicon fluoride. Percy§ has shown by experiments that, while a loss in weight does take place, the formula is wrong, as it expresses more than three times the actual amount lost. It would seem, therefore, that the basis on which these methods are founded is not a correct one. Owing to the high temperature there is always danger of losing tin through volatilisation, although|| in a charcoal-lined crucible this may be prevented by entirely excluding the air. In regard to scorification it seems doubtful whether it can be avoided so as to give satisfactory results.

(1). Ricketts¶ recommends mixing 10 grms. of ore with 10 to 20 grms. of fluor-spar or cryolite. He then says: "Charge in a charcoal-lined crucible, which is first covered with charcoal and then luted with clay, heat strongly for about one hour, remove carefully from the fire, and tap gently. Treat the button as an alloy afterwards." These instructions were closely followed, fluor-spar being used and the time of exposure to heat lengthened, as previous experiments in charcoal-lined crucibles had shown that considerable time is required for the heat to penetrate the lining.

Three experiments were made, resulting in a grey, slightly fritted mass, which contained white tin and black

tin mixed with fluor-spar. This gave, when crushed in a porcelain mortar and treated with water, grey slimes and, as residue, the mixture of white and black tin. The complete reduction of the stannic oxide was probably prevented by the intimate admixture of fluor-spar. It could scarcely have been caused by insufficient heat. A hot anthracite fire was used; the furnace was 12×12 inches, the crucible resting on 3 inches of coal, and being covered by 3 inches of coal (to the lower edge of the flue). The draught was strong, the total time of exposure to heat two hours.

(2). Rickett.* gives a similar charge for a chalk-lined crucible—ore 10 grms., fluor-spar 10 grms., powdered charcoal 2 grms., a salt and charcoal cover, and recommends a hot fire.

This method produced negative results. The charge at the bottom and sides of the crucible was fused; it was grey, showing a crystalline structure. At the bottom the fused rim was $\frac{1}{2}$ inch thick, decreasing to $\frac{1}{4}$ inch higher up. Inside this shell was a fritted mass of a colour from dark grey to black, consisting apparently of charcoal and fluor-spar, with fine particles of tin dispersed through it, and covered by a pumice-like grey slag, probably a mixture of salt and fluor-spar.

(3). Balling† recommends mixing 5 grms. of ore with 2.5 grms. of fluor-spar and 2.5 grms. of lime, charging the mixture in a charcoal-lined crucible, and treating as in the old German method of assaying iron ores in the dry way—that is, heating for an hour and a half, the last fifteen or twenty minutes at a white heat.

The result of several fusions was a slightly sintered mass of a greyish white colour collected into a button. Through it were distributed prills of metallic tin of different sizes, the largest being about the size of a small pin-head. Another negative result.

No pains was spared to make these experiments with fluor-spar as thorough as possible, and the failure to obtain satisfactory results must have been due to one of two things; either the ore used was not suited to that mode of treatment, or important particulars were omitted from the directions given.

3. *Fusion with Potassium Cyanide.*—This very valuable method of assaying tin ores is given by Mitchell.‡ In describing his manner of operating, he says he uses a 3-ounce Hessian crucible, rams into its bottom a $\frac{1}{4}$ -inch layer of potassium cyanide, adds the charge, consisting of 100 grains of ore mixed with from four to five times its weight of powdered potassium cyanide, and gives a cover of the same flux. He then heats at a moderate temperature for ten minutes, removes the crucible, taps it gently, and allows it to cool. He dissolves the slag in water to see if any reduced metal or heavy particles of the original ore are present, and says that, with ordinary care, the results are accurate to 0.5 per cent.

The basis on which the process rests can be expressed by the formula $\text{SnO}_2 + 2\text{KCy} = \text{Sn} + 2\text{KOCy}$. Potassium cyanide, being more powerful than any other reagent, acts more quickly, and also at a lower temperature, thus reducing the volatilisation of tin to a minimum. The disadvantages are its cost and its very poisonous character. The extra expense need hardly be taken into consideration, as it is very nearly counterbalanced by the saving in time, the difference being fully made up by the superiority of the results obtained. Its poisonous character requires that special care should be taken in handling it. The mortar ought to be covered with a wooden lid, having a hole through which the handle of the pestle passes, and a cloth placed over this to avoid dusting. A sponge or handkerchief should protect nose and mouth while pulverising, weighing, and mixing the reagent with the ore. The crucible should be placed to cool under a good draught, and care taken to finish the

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technological Quarterly*, Vol. iii., No. 2.

† "Traité des Essais," 1847, vol. i., p. 436.

‡ E. G. Balling, "Metallurgische Chemie," Bonn, 1882, p. 88.

§ "Metallurgy of Fuel, &c.," London, 1875, p. 80.

|| Berthier, "Traité des Essais," 1847, vol. ii., p. 458.

¶ "Notes on Assaying," 1886, p. 88.

* "Notes on Assaying," 1886, p. 89.

† "Die Probirkunde," 1879, p. 391.

‡ "Manual of Assaying," 1881, pp. 481–483.

TABLE VIII.
Resulting Tin.

No. of Assay.	Total.		In button.		In slags.		In crucibles.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
35.	3'385	67'70	3'330	66'60	—	—	—	—
36.	3'365	67'30	3'310	66'20	—	—	—	—
37.	3'355	67'10	3'300	66'00	—	—	—	—
38.	3'355	67'10	3'300	66'00	—	—	—	—
Average..	3'365	67'30	3'310	66'20	0'005	0'10	0'050	1'00

breaking of crucibles and handling of cyanide slags before the fingers have occasion to become moist. If these precautions are observed, there is no danger whatever, as the writer can testify from repeated experience.

In the experiments the ordinary chemically pure potassium cyanide—98 per cent KCy and 2 per cent KOcy—was first used; then the effects produced by the different impurities that are apt to be found in commercial cyanides are studied; and lastly, the commercial cyanides themselves were tested. The regular method given by Mitchell was varied in different ways to see what effect modifications from other methods would have on the reagent.

In regard to temperature and time required for the assay, Mitchell says "a moderate fire," which will keep the charge at a "steady fusion" for "ten minutes." It was found that a charge can be kept at a steady continuous fusion for twenty minutes, and the temperature be too low to complete the chemical reaction. Small globules of tin can be seen floating about in the slag, and these will not be collected into one button when the crucible is broken. On the other hand, the temperature may be raised so high that the charge will boil, and the fusion still be steady and continuous. The tin will be reduced, but will not collect into one button, and the assay will again be imperfect. The best way to regulate the temperature would seem to be the following. Begin with a hot fire, and keep it at the highest point to which potassium cyanide can be heated without beginning to boil and evolve heavy fumes. This temperature is easily recognisable after a few assays. Ten minutes is a very good average for the time, beginning when the charge is liquid and brown-red. An assay may be considered finished when the pure upper slag has become so transparent that the impurities contained at the bottom of the crucible are visible through it. The tin will then have collected into one button beneath the lower slag, and very few, if any, prills will be found.

The experiments with potassium cyanide were as follows (1 to 11):—

(1). 5 grms. of ore mixed with 20 grms. of potassium cyanide were charged in a Battersea crucible, size F, into the bottom of which had been rammed 5 grms. of cyanide; the charge was covered with 5 grms. of cyanide; time given, ten minutes.

The slag was as liquid as water. When cold, its surface was smooth, and had the shining lustre of porcelain. The crucible was not corroded, and the upper part was free from tin. On breaking the crucible, it was found that the potassium cyanide had filtered through nearly the entire bottom and blackened it, the blackness diminishing on the sides and disappearing near the top. The fracture of the upper slag was coarsely granular; it was opaque, milk-white, brittle, and soluble in water. On the bottom of the crucible was an amorphous, uneven slag; it had a resinous lustre, was subtranslucent, of light green colour, harder than the white slag, and insoluble in water. It was charged with the impurities contained in the ore. The button separated well from the slag, was white, bright, easily cut, malleable, and free from iron.

To examine the slags and lower part of the crucible for prills of tin, they were placed in hot water. The white slag dissolved readily, and the green, as a rule, separated easily from the crucible. The solution of potassium cyanide and cyanate was removed by decanting, and the

pieces of crucible taken out and dried apart from the residue in the dish. Both were then crushed separately, and passed through a 60-mesh sieve. The resulting fine pulp was panned, and the siftings weighed with their scales, the slags and crucibles of one series of assays being worked up together, as the weights of the resulting buttons were close enough to justify the proceeding.

Table VIII. shows that the average result is 0'54 per cent lower than that found by chemical analysis, and the percentage of tin in slags and crucible—1'10 per cent—rather higher than would have been expected. The greatest discrepancy, however, in the total weights is only 0'03 grm., but expressed in percentage it amounts to 0'6 per cent. It seemed, therefore, more advisable to use 10 grms. of ore, as in the next experiments.

(2). The charge consisted of ore, 10 grms.; potassium cyanide, 40 grms.; 5 grms. cyanide for bottom of crucible, and 5 grms. cyanide for cover; crucible, size F; time, fifteen minutes.

The only difference between the first and second assays is, that in the latter the bottom was covered with a larger quantity of green slag, showing (as the crucibles were of the same size as before) a thicker layer. In assays Nos. 35 to 38 this heavy green slag had collected around the button, filling the space between it and the crucible, and not quite reaching the top of the button, which was covered by the pure white slag. It would, therefore, seem advisable to use for a 10-grm. assay a crucible having a larger base than the size F of the Battersea make. The button could then lie on the bottom and be surrounded by the impure slag, the top being covered by pure white slag, which helps reduction and the successful collecting of the metal in one button. If the assays are made in the muffle, the 10 and 20-grm. (or Colorado A and B) crucibles, used for lead and assays, might be very suitable for the purpose.

The total average differs here only 0'35 per cent from the chemical analysis; three assays agree perfectly, and the fourth shows only 0'01 grm., or 0'1 per cent difference, which is very close. The percentage of tin in slags and crucible is half as much as that in the previous assays (Table VIII.), suggesting that the first assays, Nos. 35 to 38, might have been benefited by a longer exposure to the heat.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act, 1871.*

London, August 4th, 1890.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past

month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, 14 were found to be "very slightly turbid," the remainder being clear, bright, and well filtered.

During the first three weeks of the month of July the condition of the water supply to the Metropolis continued to be, as it had been for months previously, entirely satisfactory; but during the last ten days of the month there was manifested an appreciable deterioration, especially in respect to degree of colour-tint upon examination in bulk, consequent on the exceptional heavy rainfall of the 17th and 18th. This deterioration was noticeable to some extent in the supply of all the seven Companies, but more especially, as shown by the Tables, in the case of four out of the five Companies taking their supply from the Thames.

That the deterioration was associated with but an insignificant increase in the proportion of organic matter present in the water—and that inferred on good grounds to be mainly of a vegetable nature—is shown by a comparison of the determinations of organic carbon present in the water-supply of the earlier and later portions of the month, with the determinations of the degree of colour-tint manifested during the same periods respectively. Thus, in the case of the five Companies deriving their supply from the Thames, while the mean ratio of brown to blue tint of the water during the first three weeks of the month was as 13 : 20, during the last ten days of the month it was as 22 : 20. But as regards organic carbon, the mean proportion for the first three weeks of the month being 0.143 part in 100,000 parts of the water, with a maximum of 0.161 part in any single sample examined, the mean proportion for the last week of the month was but 0.165 part in 100,000 parts of the water, with a maximum of 0.185 part in any single sample examined. Altogether, the mean proportion of organic carbon for the entire month of July was but 0.152 part, as against a mean of 0.150 part for the month of June.

As regards the heavy rainfall of the month and consequent unfavourable condition of the rivers, it is to be noticed that on 28 out of the 31 days of the month there was an appreciable rainfall in the Thames and Lea Valleys, and on one or two of the early days of the month a decidedly heavy rainfall, followed up by the remarkable rainfall of the 17th, and very considerable rainfall of the following day. Mr. G. J. Symons, F.R.S., has informed us that the mean rainfall for the month in the Thames and Lea watersheds was 3.73 inches, of which 1.92, or nearly two inches, fell on the 17th and 18th.

Mr. Symons further writes us word: "The rain of the 17th was a very exceptional if not unprecedented one, not on account of the absolute totals (though one gauge, Lord Ebury's, at Moor Park, Rickmansworth, collected 4.19 inches, and another at Hillingdon, Uxbridge, collected 4.00 and then ran over) as because of the very large area with upwards of two inches, and the considerable area with more than three." Speaking of these high returns, he has elsewhere observed, "It is perhaps noteworthy that they are all from stations either actually on the banks of the Thames, or within three miles of it," in view of the really unprecedented amount of the rain-

fall—in regard to the wide area of heavy fall, more considerable even than that of July 26th, 1867—it is only to be wondered at that the water supply to the Metropolis should have been so inconsiderably affected.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 19th, 1890.

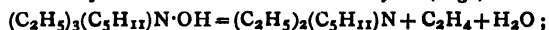
Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

(Continued from p. 97).

55. "*The Action of Heat on the Chlorides and Hydroxides of mixed Quaternary Ammonium Compounds.*" By N. COLLIE, Ph.D., and S. B. SCHRYVER, B.Sc.

The object of the authors' experiments has been to devise, if possible, a general method for preparing mixed tertiary amines. One of them (Collie, *Chem. Soc. Trans.*, 1888, 714—726) has shown that mixed tertiary phosphines could be prepared by heating the quaternary phosphonium compounds, and the following results show distinctly a marked analogy between the compounds of nitrogen and those of phosphorus.

Hofmann has already pointed out that when the hydroxides of mixed quaternary ammonium compounds containing ethyl are heated, one of the ethyl groups is invariably eliminated in the form of ethylene, e.g.,—



and Lossen has obtained similar results. But none of the mixed tertiary amines were thus prepared in a state of purity; both Hofmann and Lossen were content to reconvert the products into quaternary ammonium chlorides and analyse the platinum salts. The authors have used trimethylamine and triethylamine, and from these tertiary amines have prepared the quaternary ammonium compounds by heating the alcoholic solution of the amine with the iodide or chloride of primary, secondary, or tertiary hydrocarbon radicles of the C_nH_{2n+1} series. The action of heat on the quaternary ammonium compounds containing the radicles allyl, benzyl, and phenyl has also been studied. The mixed tertiary amines which have thus been prepared for the first time in the pure condition are:—

Dimethylethylamine, b. p.		45—46° C.
Diethylmethylamine, "		66—67° C.
Dimethylamylamine, "		113—114° C.
Dimethylbenzylamine, "		178—179° C.

56. "*Action of Phosphoric Anhydride on Fatty Acids.*" By F. STANLEY KIPPING, Ph.D., D.Sc.

The investigation of the action of phosphoric anhydride on fatty acids has now been extended to palmitic acid and lauric acid, and some preliminary experiments have also been made with caproic acid. These compounds, like stearic acid and heptylic acid, are decomposed by phosphoric anhydride at a moderately high temperature in accordance with the equation—



As the ketone produced can easily be obtained in a pure condition and the yield is also good, this method may be conveniently employed for the preparation of the compounds in question.

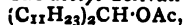
Palmitone, $(C_{15}H_{31})_2CO$, can be prepared by heating palmitic acid at 200—210° and gradually adding a slight

excess of the theoretical quantity of phosphoric anhydride. The dark brown mass is allowed to cool, treated first with water and then with soda to free it from phosphoric acid, and the residue extracted several times with boiling alcohol; on cooling, the ketone separates from the alcoholic extracts as a yellowish powder, and can be obtained in a pure condition by re-crystallising it from boiling alcohol. The yield of the pure product is more than 50 per cent of the theoretical. It is a colourless crystalline powder melting at 82–83°. The *hydroxime*, $(C_{15}H_{31})_2C:N\cdot OH$, forms peculiar fern-like crystals and melts at about 64–65°.

Dipalmitylcarbinol, $(C_{15}H_{31})_2CH\cdot OH$, is obtained by reducing palmitone with sodium in boiling alcoholic solution; it crystallises from alcohol in silky plates and melts at 84–85°. When boiled with acetic anhydride for several hours, it is converted into a colourless crystalline acetyl-derivative, $(C_{15}H_{31})_2CH\cdot OAc$, melting at 49–50°.

Laurons, $(C_{11}H_{23})_2CO$, can be easily prepared by heating lauric acid at 220–230°, with a slight excess of the theoretical quantity of phosphoric anhydride; at a lower temperature the acid is not readily decomposed. The product is purified as described in the case of palmitone; the yield is about 40 per cent of the theoretical. The *hydroxime*, $(C_{11}H_{23})_2C:N\cdot OH$, is formed when the ketone is heated with hydroxylamine hydrochloride and excess of potash in dilute alcoholic solution; it crystallises from alcohol in slender needles and melts at 39–40°.

Dilaurylcarbinol, $(C_{11}H_{23})_2CH\cdot OH$, is obtained when the ketone is reduced with sodium and water in ethereal solution; it crystallises in colourless waxy plates and melts at 75–76°. The acetyl derivative,—



is formed when the alcohol is boiled with acetic anhydride for some hours; it crystallises from methyl alcohol in colourless plates melting at 34–35°.

Caproic acid, at its boiling-point, is decomposed by phosphoric anhydride, giving the ketone $(C_5H_{11})_2CO$; the product can be isolated by distillation with steam. The yield seems so be fairly good.

57. "*aa'-Dimethyl-aa'-diacetylpentane*." By F. STANLEY KIPPING, Ph.D., D.Sc., and J. E. MACKENZIE, B.Sc.

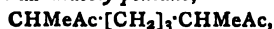
The conversion of *aa'*-diacetylpentane into dimethyl-dihydroxyheptamethylene on reduction (Kipping and Perkin, *Proc. Chem. Soc.*, 1889, 145) being an action to which much interest attaches, the authors have instituted experiments with a view to ascertain whether other diketones of analogous constitution can be converted into heptamethylene derivatives in a similar manner. The investigation is not yet completed, but *aa'*-dimethyl-*aa'*-diacetylpentane and various other compounds have already been prepared.

Ethyl-aa'-dimethyl-aa'-diacetylpimelate,—



can be obtained by treating ethylic methylacetoacetate with trimethylene bromide and sodium ethoxide in absolute alcoholic solution; a considerable quantity of compounds of lower boiling-point is also formed, so that the yield of ethylic dimethyldiacetylpimelate is only 50–60 per cent of the theoretical. It is a colourless oil boiling at about 250° under a pressure of 60 m.m. On hydrolysis with alcoholic potash the ethereal salt is decomposed into dimethyldiacetylpentane, dimethylacetylcaproic acid, and dimethylpimelic acid, the relative quantity of each of these three compounds depending to a considerable extent on the concentration of the alcoholic potash, and on the manner in which the hydrolysis is carried out.

aa'-Dimethyl-aa'-diacetylpentane,—



is a colourless oil boiling at 198–201° under a pressure of 112 m.m.; it shows no signs of crystallising even when cooled to 0°. The *dihydroxime*,—



crystallises from a mixture of benzene and light petroleum in colourless needles melting at 95–95°.

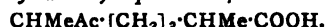
aa'-Dimethylpimelic acid,—



separates from light petroleum in compact colourless crystals, and melts at 74–75°; it is readily soluble in water and most organic solvents. The *silver* salt, $C_9H_{14}O_4Ag_2$, is a colourless, seemingly amorphous compound, only sparingly soluble in boiling water.

Ethyl-aa'-dimethylpimelate, $C_9H_{14}O_4Et_2$, is formed in large quantities when ethylicmethylacetoacetate is treated with sodium ethoxide and trimethylene bromide in alcoholic solution in presence of a small quantity of water; under these conditions the ethylic dimethyldiacetylpimelate which is produced in the first case seems to be completely converted into the ethylic dimethylpimelate. It is a colourless oil boiling at 190–191°. On hydrolysis with alcoholic potash it is converted into dimethylpimelic acid.

aa'-Dimethyl-ω-acetylcaproic acid,—



is a thick colourless oil boiling at about 218–220° under a pressure of 60 m.m.; it cannot easily be obtained in a pure condition.

58. "*Berberine*." Part II. By W. H. PERKIN, jun. Ph.D., F.R.S.

In Part I. of this research (*cf. Chem. Soc. Trans.*, 1889, 63) the results of preliminary experiments on the oxidation of berberine with varying quantities of potassium permanganate were briefly described, and a short account of some new substances obtained during these experiments appended. In the further prosecution of this research very large quantities of the alkaloid have been oxidised. The amounts used in the experiments varied considerably, but some of the best results were obtained where, in each operation, 7 grms. of berberine, 9 grms. of potassium permanganate, and about 1 gm. of potassium carbonate were used. The product from a number of such operations was treated with sulphur dioxide until the whole of the manganese precipitate had been brought into solution; the resulting yellow precipitate was then separated from the yellow solution (A) by filtration, washed with water, and warmed to 40° with a dilute sodium carbonate solution, by which means about one-half of the precipitate was dissolved (B).

The insoluble residue contains, besides two substances—berberilic anhydride, $C_{20}H_{17}NO_8$ (m. p. 236–237°), and berberal, $C_{20}H_{17}NO_7$ (m. p. 150°)—which have been already described, a new base, $C_{20}H_{19}NO_9$, which is very sparingly soluble in water, and crystallises in flat yellow plates, and small quantities of two other substances.

The alkaline solution (B) contains, as principal product, α -berberilic acid, $C_{20}H_{19}NO_9$, which was described in the former paper. This acid, when heated to 180°, is converted into berberilic anhydride; in other respects it shows great similarity to β -berberilic acid, which is described below.

The solution (A) was evaporated in large flat basins to about half its bulk, filtered from the precipitate (C) which separates and then evaporated to a small bulk (D). The precipitate (C) was warmed with dilute chlorhydric acid till free from inorganic matter, the residue washed with water, dried, and extracted with hot acetic acid, by which means a quantity of berberilic anhydride was removed. The insoluble residue was dried and dissolved in a small quantity of boiling aniline, from which solution it was deposited, on cooling, in glittering yellow plates, having the composition $C_{20}H_{17}NO_6$.

This substance, which is formed in very small quantities, has only been superficially examined. It is characterised by its insolubility in the usual solvents, and by the fact that it yields a beautifully crystalline potassium salt when dissolved in alcoholic potash.

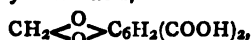
The highly concentrated liquors (D) were extracted 30

times with ether, the ether evaporated and the semi-solid residue boiled with water until the greater part had dissolved (E). The residue dissolved almost entirely in dilute sodium carbonate solution (P), leaving a dark brown pasty residue, from which, by treatment with glacial acetic acid, a substance crystallising in long brown needles can be isolated. This substance melts at 167°, and has the formula $C_{20}H_{15}O_5$, and dissolves in alkali with formation of an acid, which crystallises from water in long glittering needles, m. p. 147°.

The alkaline solution (F) acidified with chlorhydric acid, deposits a brown amorphous precipitate, which crystallises from glacial acetic acid in glittering colourless plates, which melt at 200° with decomposition and charring.

This substance, which has the composition $C_{20}H_{15}NO_7$, is a monobasic acid, yielding highly characteristic salts, of which the silver salt, $C_{20}H_{14}NO_7Ag$, was analysed. The calcium, lead, and zinc salts are sparingly soluble, but beautifully crystalline.

The solution (F) was next examined. This was heated to boiling, rendered slightly alkaline with sodium carbonate, and allowed to stand twenty-four hours. At the end of this time the liquid is found to be filled with a mass of glittering plates of a new base, $C_{10}H_9NO_3$, which will be described in detail later on. These are filtered off, the alkaline solution neutralised with chlorhydric acid, and mixed with an excess of strong solution of calcium chloride. No precipitate is produced in the cold, but on boiling, a crystalline calcium salt separates. This is collected, washed with a little water, dissolved in hot dilute hydrochloric acid, from which solution, on standing, a quantity of crystals separate. These crystals are a mixture of two acids, which both melt at 18°, and which can be separated by re-crystallisation from water. The more soluble acid is hemipinic acid. The second acid crystallises from water, without water of crystallisation, in colourless plates, which, on analysis, give numbers agreeing with the formula $C_6H_6O_6$. The silver salt has the composition $C_6H_4O_6Ag_2$. This acid is most probably identical with hydrastric acid,—



which Freund and Lachmann (*Berichte*, xxii., 2324) obtained from hydrastrinine, and which melts at 175°.

The following are the results of the examination of the principal products described above:—

1. *Berberilic anhydride*, $C_{20}H_{17}NO_8$, m. p. 236—237°, does not combine with phenyl hydrazine. When boiled with acetic anhydride for some hours it is converted into an acetate, $C_{20}H_{16}NO_7(C_2H_3O_2)$, which crystallises from acetic anhydride in hard light yellow prisms melting at 140°. Boiling dilute sulphuric acid decomposes this acetate quantitatively into berberilic anhydride and acetic acid. Pentachloride of phosphorus converts berberilic anhydride into a chloride, $C_{20}H_{16}NClO_7$, which crystallises from benzene in hard garnet-red prisms melting at 167°. This substance is readily acted on by water and re-converted into berberilic anhydride. Berberilic anhydride dissolves readily in warm dilute caustic soda solution, with formation of β -berberilic acid, which is precipitated on the addition of acids as a white sticky mass, which becomes hard on standing.

This new acid crystallises from dilute alcohol in warty masses, and melts at 180°, being at this temperature re-converted into its anhydride. Its composition is—



and it is isomeric with α -berberilic acid, which melts at about 140°.

A number of salts were prepared by precipitating a neutral solution of the ammonium salt with various agents. These salts, however, are not derived from berberilic acid, $C_{20}H_{19}NO_9$, but all contain one molecule of water less, and are therefore derivatives of the anhydride $C_{20}H_{17}NO_8$. The silver salt, $C_{20}H_{16}AgNO_8$, is a white

amorphous mass. The methylic salt, $C_{20}H_{16}(CH_3)NO_8$, prepared by the action of methyl iodide on the silver salt, crystallises from acetic acid in glittering plates, which melt at 178—179°. As it was thought possible that the methyl group might be attached to nitrogen, the action of hydrogen iodide on this methyl salt was investigated, and it was found that three methoxy-groups were present, two belonging to the berberine molecule. The substance is therefore a true methylic salt.

The most important reaction of β -berberilic acid is the change which this substance undergoes on hydrolysis. When boiled with dilute sulphuric acid (5 per cent), it dissolves completely, being converted quantitatively into hemipinic acid and a new base:—

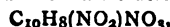


small quantities of berberilic anhydride being always re-generated during the decomposition.

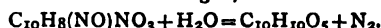
After extracting the hemipinic acid by ether, the sulphuric acid liquors are evaporated to a small bulk, and then allowed to stand forty-eight hours, when the sulphate of the base separates in large slightly brownish coloured tablets. These are collected, dissolved in water, treated by the calculated quantity of baryta-water, and the solution gently evaporated. The concentrated solution deposits the base in large flat monoclinic plates which melt at 180—182°, and contain 1 mol. of water. The platinumchloride, $(C_{10}H_{11}NO_4HCl)_2PtCl_4$, crystallises from water in dark yellow needles which melt at about 220°. Nitrous acid converts the base into a substance of the formula $C_{10}H_8O_4$, which will be described later on.

When heated to 180°, or digested with strong potash solution, or even simply boiled with water for some time, the base loses the elements of a molecule of water, and is converted into another base, $C_{10}H_9NO_3$.

This important substance crystallises from water in magnificent colourless glittering plates which melt at 182°. It is feebly basic, its salts being only stable in the presence of large quantities of acid. It is a very stable substance, and when boiled with dilute nitric acid is principally converted into a nitro-derivative,—



which crystallises from water in yellow plates, m. p. 175—180°. If the base be dissolved in a large quantity of dilute chlorhydric acid (HCl to $2H_2O$), well cooled, and the calculated quantity of sodium nitrite (1 mol. prop.) added, an immediate precipitate of a yellow nitroso-compound, $C_{10}H_8(NO)NO_3$, is produced. This crystallises from alcohol in glittering yellow needles which melt at 195—196° with decomposition. When boiled with dilute caustic soda, this nitroso-compound rapidly dissolves with evolution of nitrogen,—



The new substance melts at 146°, and is readily soluble in hot water and most of the usual solvents. It is an acid, the salts of which are fairly characteristic. The silver salt, $C_{10}H_9AgO_5$, is crystalline, and soluble in hot water. When heated to 150°, or boiled with water, this substance readily loses 1 mol. of water, and is converted into its anhydride, $C_{10}H_8O_4$.

This substance crystallises from water in large flat plates which melt at 126°, and distils almost without decomposition. It is re-converted by dissolution in alkalies into the acid $C_{10}H_{10}O_5$. Nitric acid produces a light yellow mononitro-compound, $C_{10}H_7(NO_2)O_4$, which melts at 197°. A number of experiments were tried with the object of oxidising the molecule to some well known acid, but without success, the substance being either unacted on or else completely destroyed by the oxidising agents employed. Gently fused with potash, the substance yields a mixture of pyrocatechol and protocatechuic acid.

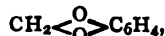
When heated with hydriodic acid in Zeisel's apparatus, no trace of methyl iodide was evolved, a proof that the molecule contains no methoxyl-groups; chlorhydric acid (HCl to $4H_2O$) at 170—175° decomposes the substance,

however, and apparently quantitatively, with deposition of carbon and formation of a new compound,—

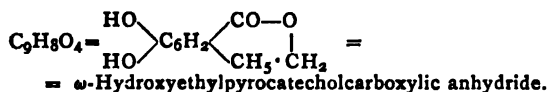
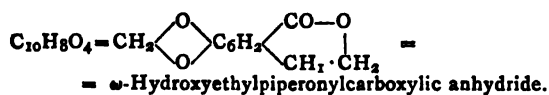
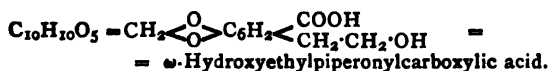
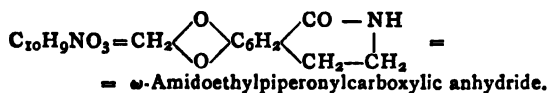
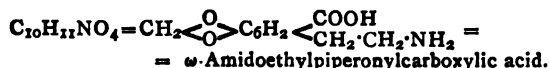


This compound crystallises from water, in which it is very soluble, in warty masses which melt at about 220–225°. Its aqueous solution shows with ferric chloride the most intense pyrocatechol reaction; it gives a white precipitate with acetate of lead, and reduces both Fehling's solution and ammoniacal nitrate of silver.

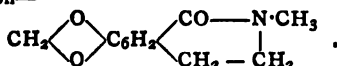
The result shows that all these derivatives contain the piperonyl-group,—



the constitution and proposed nomenclature of these substances being apparent from the following table:—



Freund and Will (*Berichte*, xx., 2400), in their researches on hydrastine, describe a substance, oxyhydrastine, obtained by the action of caustic potash on hydrastine, which they subsequently prove to have the constitution—



If the formulæ assigned to the compounds above be correct, this oxyhydrastine must be a methyl-derivative of the compound $C_{10}H_9NO_3$, and in order to confirm these formulæ every effort was made to convert the substance $C_{10}H_9NO_3$ into oxyhydrastine.

The experiments first made in this direction are the following:—

1. $C_{10}H_9NO_3$ and $C_{10}H_{11}NO_4$ were treated with methyl iodide under various conditions, with and without the addition of alkali.

2. $C_{10}H_8O_4$ was heated with methylamine and with methylamine acetate in a sealed tube.

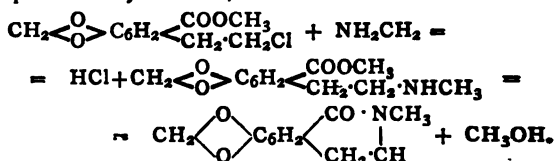
3. $C_{10}H_{10}O_5$ was converted into the methylamine salt, and this was distilled.

But all these experiments failed to produce the change desired. The transformation was, however, ultimately accomplished in the following way:—The compound $C_{10}H_8O_4$ is converted by phosphorus pentachloride into the chloride $C_{10}H_7O_4Cl$, which crystallises from chloroform in glittering needles melting at 159°. This substance is remarkable for the ease with which it loses hydrogen chloride, and is re-converted into $C_{10}H_8O_4$. This change takes place on heating to 150°, or on heating with alkalis, or reducing with zinc-dust and acetic acid, and also on heating with methylamine in alcoholic solution in a sealed tube.

In order to prevent this, the carboxyl-group was protected by converting the chloride into its methylic salt. For this purpose, $C_{10}H_7O_4Cl$ was treated in chloroform

solution with an excess of pentachloride of phosphorus, the chloroform distilled off, and the residue poured into methyl alcohol. The methylic salt was thus obtained as a white powder, which crystallised from dilute methyl alcohol in beautiful woolly tufts of needles melting at 83°.

When this was heated with methylamine in alcoholic solution at 130° for six hours and the product was boiled with alcoholic potash, oxyhydrastine was almost quantitatively obtained, thus:—

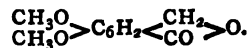


The substance obtained in this way melted at 98°, and showed all the properties of oxyhydrastine.

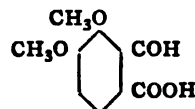
2. *Berberal*, $C_{20}H_{17}NO_7$, m. p. 150°.—When in a finely divided state and very pure, berberal is moderately readily hydrolysed by boiling dilute sulphuric acid (containing 20 per cent H_2SO_4), a clear slightly brownish coloured solution resulting. Ether extracts from this solution a colourless crystalline mass, which, when treated with dilute sodium carbonate, is separated into the base $C_{10}H_9NO_3$, described above, and a new acid. This latter substance crystallises from water in beautiful long satiny needles which melt at 121°, and on analysis give numbers agreeing with the formula $C_{10}H_{10}O_5$. The analysis of the silver salt, $C_{10}H_9AgO_5$, showed the acid to be monobasic. When treated with hydrogen iodide in Zeisel's apparatus, results were obtained which proved that the acid contained two methoxyl groups. Fusion with potash converts the acid into protocatechuic acid; but if caustic potash solution (sp. gr. 1.4) be employed and the acid simply digested with this on a reflux apparatus, an almost quantitative yield of veratric acid, $(CH_3O)_2C_6H_3COOH$ (m. p. 177–178°), is obtained.

When subjected to the action of hydroxylamine in alkaline solution at ordinary temperatures, a hydroxime, $C_{10}H_{11}NO_5$, is produced. This crystallises in fine needles, which, when heated, melt at 124°, but at once become solid again, and then do not again melt till the temperature is raised to 213°. In order to investigate this decomposition, the pure hydroxime was heated to 180° for fifteen minutes and the residue re-crystallised from alcohol. Beautiful needles were thus obtained which melted at 224–226°, and were readily identified as hemipinimide.

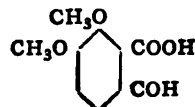
The acid $C_{10}H_{10}O_5$ is readily reduced by sodium amalgam, being converted into an acid which, when precipitated from its alkaline solution by the addition of an acid, at once loses water with formation of pseudomekonin,—



This substance crystallised from water in long needles melting at 122–123°, and possessed all the properties ascribed to pseudomekonin by Solomon (*Ber.*, xx., 884). These experiments prove conclusively that the acid $C_{10}H_{10}O_5$ has the constitution represented by the formula—

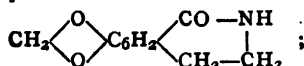


and it thus bears a very close relationship to opianic acid,—

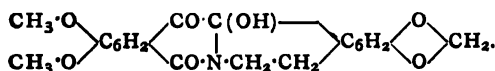


which is brought out in a most interesting way by a parallel study of the reactions of the two substances; thus, for instance, on reduction both yield mekonins, and with hydroxylamine both yield hydroximes, which, when gently warmed, are converted into hemipinimide. The acid $C_{10}H_{10}O_5$ may therefore be called *pseudopianic acid*.

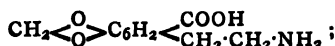
These experiments throw considerable light on the constitution of *berberal*. This substance on hydrolysis yields pseudopianic acid and the base—



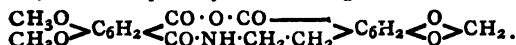
its constitution is therefore probably represented by the formula—



Berberilic anhydride, $C_{20}H_{17}NO_8$, yields on hydrolysis hemipinic acid and the base—



it has, therefore, possibly the following constitution:—



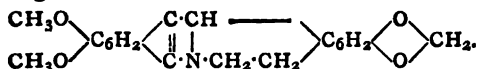
These experiments also show:—

1. The nature of all the oxygen atoms in the molecule of berberine, $C_{20}H_{17}NO_4$, thus precluding the hypothesis that berberine owes its colour and tintorial power to the presence of a quinone-group.

2. That berberine is an isoquinoline-derivative.

3. That berberine is closely related to hydrastine, narcotine, and papaverine.

Further experiments must decide the question of the exact constitution of berberine; but the author is of the opinion that the following formula explains well all the reactions of this alkaloid which have hitherto been investigated:—



The discussion of this formula will be attempted in the detailed paper.

(To be continued).

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, July 7, 1890.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Thomas Townsend Bucknill, Q.C.; Edward A. Harvey; Malcolm Morris, F.R.C.S.; and William Thomas Rabbits, F.L.S.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

The Gas and Water Companies Directory, 1890. Edited by C. W. HASTINGS. London: Hazell, Watson, and Viney, Limited.

THIS work is of less interest from a technical or a sanitary point of view than are its companion volumes. But it is certain to be of great value to persons investing in gas and water undertakings, or, as the editor puts it, "to all interested in the great question of supplying light and water for the public benefit." It might here well be asked

how many promoters, directors, or shareholders of such undertakings think of the "public benefit" at all, or of anything save the great question of dividends.

Several new features have been added to the work which will increase its value. It appears that enquiries have often been made by secretaries, managers, &c., as to the amount paid by gas and water undertakings for taxation, local and national. Whether such officials think that their respective companies are too heavily taxed is a point upon which we cannot enter.

Another feature is a directory of firms supplying articles likely to be needed by gas and water undertakings.

The third, and we must say the most important, novelty is an "Electric Lighting Section." If we take a page of this section we find it divided into the following columns: Name of town; name and address of company (if not municipal); date of formation; capital; system; capacity; price per unit; name of secretary; name of electrician in charge; and area of supply, with remarks. Fifty-six towns or municipal districts are already provided with electric lights or the necessary installations are in a very advanced state.

Gas Works Statistics, 1890. Edited by C. W. HASTINGS.

London: Hazell, Watson, and Viney, Limited.

COMPANIES and towns have responded much more generally to the editor's request for information concerning their gas-production than touching their water supplies. Many of the returns are made up only to a rather remote date; thus Castleford, Chertsey, and Chigwell only carry their accounts down to 1884, whilst Dartford and Grant-ham go merely to 1883.

Some towns have worked very neatly, consuming exactly as much gas as they made in the year. Chatteris does better still; it made 3161 thousand feet of gas and sold 3486. Whether the extra 325 thousands were gas remaining in stock from a former season or air which had leaked in it does not appear.

The general illuminating power of gas has improved of late years. Berwick heads the list with 30 candle-power, followed by Liverpool with 21½, and Mallock Bridge with 21, and twenty towns dispense 20 candle gas, whilst 19 and 18 are fairly common. Nevertheless not a few places keep to the good old rule of 14 candles.

In Scotland the quality of the gas is much higher than in England. Highest comes Colinsburgh with its 65 candle gas, made from oil. In 27 towns the standard is 30 or upwards, in no case does it fall as low as 20. With the single exception of Berwick the best English gas falls short of the poorest in Scotland.

In Ireland the quality of the gas is equal, on the average, to that of England. Larne takes the lead with 22 candle gas; 14, the lowest figure, occurs very rarely.

It does not appear that in any of the three kingdoms the price of gas is a function of its illuminating power.

The Water Works Statistics, 1890. Edited by C. W. HASTINGS. London: Hazell, Watson, and Viney.

As in former years certain towns still neglect or decline to furnish information to this publication. Among the defaulting places are Aylesbury, Tring, Durham, and Kingston-on-Thames. Two new columns have been added, showing "storage capacity" and "daily consumption per head," but on these points a majority of the towns are silent. The latter piece of information, when procurable, would be very useful in calculating the dry-weather flow of sewage. Concerning the value of the column "Death rate," we are not free from doubts. No one, of course, questions the danger of polluted water. But the factors which affect the sanitary condition of a community are so many and so varied that we do not feel free to argue from the death-rate to the comparative merits of hard and soft waters.

The information concerning the water-supplies of Scottish, Irish, and Welsh towns is somewhat meagre, and is mixed up with returns from foreign parts, but only, it would appear, from towns which are supplied by English water companies.

A foot-note on p. 6 is a curiosity. We are told that a certain water "requires to be hardened," but we cannot trace to what town this note refers. We are inclined to say that no water requires to be hardened except it contains free alkali, and to harden such a water usefully would be a difficult matter.

The information under the head "Source of Supply" is still somewhat promiscuous. Some towns tell us, sensibly enough, that their wells or springs are in the chalk, the greensand, the new red, or the millstone grit, as the case may be. Others curtly say "springs," "gathering grounds," "wells," &c., without stating the geological formation. Such answers are not of the slightest value.

We are still of opinion that the statistics might be exceedingly valuable if municipalities and companies would loyally coöperate with the editor.

Might we suggest that statistics of sewage treatment—whether irrigation, filtration, or precipitation, and in the two latter cases by what process—would form a very useful companion pamphlet.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 6, August 11, 1890.

Equilibria and Reciprocal Displacements of the Volatile Alkalies.—M. Berthelot.—If the initial bodies or products undergo no dissociation, and if they are in conditions favourable for setting the reactions on foot, the magnitude of the heats liberated alone determines the phenomena. But if certain of the initial bodies or products are capable of dissociation, the existence and the degree of this dissociation must be taken into account. If we have, e.g., a salt in solution but in part dissociated into free base and a free acid, the whole forming a system in equilibrium; if we add another base then, whatever may be its relative strength, it will necessarily tend to seize the fraction of free acid resulting from the dissociation of the antagonistic salt. In consequence, the primitive equilibrium will be disturbed and a new dose of the initial salt will be dissociated, reproducing some proportion of acid, which in turn will be taken up by the second base. If the salt of the second base is capable of being eliminated by insolubility or volatility the laws of Berthelot come into action.

Death of M. Chancel.—The Secretary announced to the Academy the decease of M. Chancel, Correspondent of the Section of Chemistry, which took place at Montpellier, August 5, 1890.

Certain Novel Hydrates of Gas.—M. Villard.—The author has previously indicated the existence of solid hydrates of methane and ethane, and he has now experimented on their higher homologue, propane, which he has prepared by the method of Prof. Schorlemmer. He finds it difficult to obtain a pure hydrate by compression. The compound obtained presents at 0° a dissociation temperature bordering upon one atmosphere, and it may be preserved indefinitely below 8.5° under suitable pressures. An admixture of air has no influence upon the temperature of destruction of this hydrate, which is still 8.5°, even under strong pressures. The critical tem-

perature of the hydrates formed by methane, ethane, and propane, falls if we pass from a carbide to its higher homologue; the compounds are destroyed respectively at 21.5°, 14.5°, and 8.5°. It is sufficiently proved that carbon tetra- and di-fluoride, methylene fluoride, and fluoroform, can yield with water four solid hydrates having the respective destruction temperatures 20.4°, 10.5°, 17.6°, and 21.8°.

A New Fatty Acid.—E. Gérard.—The fatty acid in question is obtained from the seeds of *Datura stramonium*. Its composition answers to the formula $C_{24}H_{48}O_4$. The acid is, in its properties, intermediate between the palmitic and the stearic, though its melting-point is decidedly lower than that of the more fusible of its two homologues. The author proposes for it the name daturic acid.

Researches on the Purple of *Purpura capillus*.—Augustin Letellier.—At the moment when the colouration appears in the coloured band in the body of this mollusc an offensive and penetrating odour is given off which contains sulphur, and behaves with sulphuric acid and with water like allyl sulphide. No ammoniacal salts are present, but there exists a cyanide or a sulphocyanide, and the presence of carbamides or sulphocarbamides may be suspected.

Revue Générale des Sciences Pures et Appliquées.

Vol. i., No. 14, July 30, 1890.

Annual Review of Pure Chemistry.—E. Etard.—In this summary the author calls attention to the revived interest in general or physical chemistry which has characterised the last few years. The questions of dissociation, of thermo-chemistry, of electrolysis, and chemical optics have given scope for much valuable research. A most important development is that chemists now feel it to be unphilosophical to imagine atoms or molecules fixed on a surface without thickness, and enlarging the notion of relative progression, they have come to admit formulæ in space, thus recognising the study of stereochemistry. It is now found that by the simple inspection of a constitutional formula we may foretell whether the body is or is not endowed with a rotatory power. In a chapter on inorganic chemistry the author complains that in a life which is continually becoming harder the brain-working classes have no longer time for trains of research which are of necessity slow. He points out how the groups of the cerium and the yttrium metals tend to dislocate the classification of Prof. Mendeleeff. In organic chemistry M. Etard mentions the numerous transitions which have been effected between the fatty and the aromatic series, and he calls attention to the curious fact that no polygon of more than six sides has been found to exist.

THE MASON COLLEGE, BIRMINGHAM.

SESSION 1890-91.

Faculties of Arts and Science.

The next SESSION commences on Tuesday, September, 30, 1890. A SYLLABUS containing full information as to the various Courses of Instruction, Lecture Days and hours, Fees, Scholarships, &c., is published by Messrs. Cornish, New Street, Birmingham, price 6d., post free, 8d. Further particulars may be obtained on application to the Secretary, at the College.

R. S. HEATH, Principal.
GEO. H. MORLEY, Secretary.

ST. PAUL'S SCHOOL.—An Examination for filling up about Fifteen Vacancies on the Foundation will be held on the 10th September next.—For information apply to the Bursar, St. Paul's School, West Kensington.

FOR SALE.—THE CHEMICAL GAZETTE. Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

THE CHEMICAL NEWS.

Vol. LXII. No. 1606.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

LEEDS, 1890.

INAUGURAL ADDRESS OF THE PRESIDENT,

SIR FREDERICK AUGUSTUS ABEL,
C.B., D.C.L. (Oxon.), D.Sc. (Cant.), F.R.S., P.P.C.S.
Hon. M.Inst.C.E.

MANY who had the pleasure of listening last year, at Newcastle, to the interesting and instructive Address of the President to whom I am a most unworthy successor, could not fail, both by the chief subject of his discourse and by the circumstance of the official position which he occupies with so much benefit to science and the public, to have their thoughts directed to the illustrious naturalist whose philosophical Address delighted the members of the Association and the people of Leeds thirty-two years ago.

More than one-half the period of existence of this Association has passed since Richard Owen presided over its meeting in this town. Alas! what gaps have been created in the ranks of those who then were prominent for activity in advancing its work; the then General Secretary, Sir Edward Sabine; the all-popular Assistant-general Secretary, John Phillips; the Treasurer, John Taylor, now live with us only through their works and the enduring esteem which they inspired. But very few of those who held other prominent positions at that meeting have survived to see the Association re-assemble in this town. Whewell, Herschel, Hopkins, the elder Brodie, Murchison, William Fairbairn, all Presidents of Sections in 1858, have long since been removed from among us; and the then President of Section F, Edward Baines, a much-honoured and highly-talented son of the "Franklin of Leeds," whom we had hoped to count among those Vice-Presidents representing the City on this occasion, has recently passed away, in his ninetieth year, after a most honourable and useful career, during which he especially distinguished himself by his successful exertions in the advancement of the great educational movements of his time.

The illustrious President of our last meeting here, concerning whose health the gravest apprehensions were not long since entertained, is happily still preserved to us; still intellectually bright at the ripe age of eighty-six, and still, with the keen pleasure of his early life, following the progress of those branches of scientific research which have constituted the favourite occupations and the arena of many intellectual triumphs of a long career of ardent and successful devotion to the advancement of science.

To not a few of those who have flocked to Leeds to attend the annual gathering of this Association, our present meeting-place is doubtless known chiefly by its proud position as one of the most thriving manufacturing towns of the United Kingdom; of ancient renown, especially in connection with one of the chief industries identified with Great Britain in years past. But this good town of Leeds, whose cloth market was described by Daniel Defoe, one hundred and sixty odd years ago, as "a prodigy of its kind, and not to be equalled in the world," and whose present position in connection with divers of our great industries would have equally excited the enthusiasm of that graphic writer, is famous for other

things than its prominent association with manufactures and commerce.

Not many of our great industrial centres can boast of so goodly an array, upon the scroll of their past history, of names of men eminent in the Sciences, the Arts and Manufactures, in Divinity and Letters, and in heroic achievements such as are identified with Leeds and its immediate vicinity: Thomas, Lord Fairfax, one of the most prominent heroes of the Commonwealth; Smeaton, an intellectual giant among engineers; William Hirst and John Marshall, illustrious examples of the men who by their genius, energy, and perseverance placed Great Britain upon the pinnacle of industrial and commercial greatness which she so long occupied unassailed; Richard Bentley, the eminent classic and divine; John Nicholson, the Airedale poet; John Fowler and Peter Fairbairn, worthy followers in the footsteps of Smeaton; Isaac Milner, weaver and mathematician, afterwards Senior Wrangler, Smith's prizeman, Jacksonian Professor, President of Queen's College, Vice-Chancellor of Cambridge University, Dean of Carlisle, and a most illustrious Fellow of the Royal Society; Thoresby, antiquarian and topographer; Benjamin Wilson, painter, and industrious contributor to the development of electrical science; William Hey, the eminent surgeon, and friend and counsellor of Priestley; Sadler, political economist and philanthropist; the Brothers Sheepshanks—Richard, the astronomer, and John, the accomplished patron of the arts, and munificent contributor to our national art treasures; Edward Baines, whose conspicuous talents and energy developed a small provincial journal into one of the most powerful public organs of the country; his talented sons, of whom not the least conspicuous and highly respected was the late Sir Edward Baines. I might swell this voluminous list by reference to illustrious members of such families as that of Denison, of Beckett, of Lowther, but the men I have referred to fitly illustrate the remarkable array of worthies whose careers have shed lustre upon the town in or near which they were born. Yet that illustration would be altogether incomplete if I failed to speak of one whose career and works alone would suffice to place Leeds in the foremost rank of those English towns which can claim as their own men whose course of life and whose achievements have secured their pre-eminence among our illustrious countrymen. Needless to say that I refer to Joseph Priestley, born within six miles of Leeds, whose name holds rank among the foremost of successful workers in science: who, by brilliant powers of experimental investigation, rapidly achieved a series of discoveries which helped largely to dispel the shroud of mystery surrounding the art of alchemy, and to lay the foundation of true chemical science. An ardent student of the classics, of Eastern languages, and of divinity, a zealous exponent of theological doctrines which marred his career as divine and instructor, he early displayed conspicuous talents for the cultivation of experimental science, which he pursued with ardour under formidable difficulties. His acquaintance with Franklin probably developed the taste for the study of electric science which led him to labour successfully in this direction; and the publication, in 1767, of his valuable work on "The History and Present State of Electricity, with Original Experiments," secured him a prominent position among the working Fellows of the Royal Society. His connection with the Mill Hill Chapel, in 1768, appears to have given rise accidentally to his first embracing the experimental pursuit of what formerly was termed pneumatic chemistry, the foundation of which had been laid by Cavendish's memorable contribution, in 1766, to the *Philosophical Transactions*, on carbonic acid and hydrogen. Priestley's first publication in pneumatic chemistry, on "Impregnating Water with Fixed Air" (carbonic acid), attracted great attention; it was at once translated into French, and the College of Physicians addressed the Lords of the Treasury thereon, pointing out

the advantages which might result from the employment, by men at sea, of water impregnated with carbonic acid gas, as a protective against, or cure for, scurvy.

Six years later, Priestley investigated the chemical effects produced on the air by the burning of candles and the respiration of animals, and, having demonstrated that it was thereby diminished in volume and deteriorated, he showed that living plants possessed the power of rendering air, which had been thus deteriorated, once more capable of supporting the combustion of a candle. At about this time Priestley received very advantageous proposals to accompany Captain Cook upon his second expedition to the South Seas; but when about to prepare for his departure he learned from Sir Joseph Banks that objections against his appointment, on account of the great latitude of his religious principles, had been successfully urged by some ecclesiastical member of the Board of Longitude. In 1773 the Royal Society awarded Priestley the Copley Medal for a remarkable paper entitled "Observations on Different Kinds of Air," and in that year he became librarian and literary companion to the Earl of Shelbourne (afterwards Marquis of Lansdowne), and thereby secured special advantages in the pursuit of his scientific researches.

With respect to his departure from Leeds, he expressed himself as having been very happy there "with a liberal, friendly, and harmonious congregation, to whom my services (of which I was not sparing) were very acceptable. Here I had no unreasonable prejudices to contend with, so that I had full scope for every kind of exertion; and I can truly say that I always considered the office of a Christian minister as the most honourable of any upon earth, and in the studies proper to it I always took the greatest pleasure." During the next five years he published as many volumes describing the results of important experiments on air. After investigating the properties of nitric oxide, and applying it to the analysis of air, Priestley, in 1774, discovered and carefully studied oxygen, which he obtained by the action of heat upon the red oxide of mercury. He was the first to prepare and study sulphurous acid, carbonic oxide, nitrous oxide, hydrochloric acid (*marine acid air*), and the fluoride of silicon, and carried out important researches on the properties of hydrogen, and of other gases previously but little known. His great quickness of perception and power of experiment led him to the achievement of many novel and important results; but one cannot help contrasting his somewhat random search after new discoveries with the close logical reasoning and philosophic spirit which guided and pervaded the remarkable researches of him whose departure from amongst us since the last gathering of this Association is so universally deplored—of the great discoverer of the universal law of the conversion of energy, James Prescott Joule. I could not add to the judicious and graceful reference to his work which Sir Henry Roscoe was privileged to make, in the last year of that philosopher's valuable life, when presiding over the recent meeting of the Association in the town which glorified in numbering Joule among its citizens; but I may, perhaps, be permitted to express the sanguine hope that the desire of the scientific world to secure the establishment of an international memorial fitly commemorative of his great life-work may be realised in the most ample manner.

The wide scope of the admirable discourse delivered by Owen in this town thirty-two years ago affords an interesting illustration of the delight which men whose best energies are devoted to the cultivation of one particular branch of science take in the results of the labours of their fellow workers in other departments, and in their achievements in contributing to the general advancement of our knowledge of Nature's laws and of their operations. It is to this bond of intimate union between all workers in pure science that we owe the instructive reviews of the progress made in different departments of science, with

which we have often been presented at our annual gatherings. On the other hand, those men, from time to time selected to fill the distinguished office of President, whose lives have been mainly devoted to the practical utilisation of the results of scientific research, and to the extension in particular directions of the consequent resources of civilisation, seize with keen pleasure the opportunity afforded them of directing attention to the triumphs achieved in the application, to the purposes of daily life, of the great scientific truths established by such illustrious labourers in the fields of pure science as Newton, Dalton, Faraday, and Joule. The wide and constantly extending domain of applied science presents, even to the superficial observer, a continually varied scene; not a year passes but some great prize falls to the lot of one or other of its explorers, and some apparently insignificant vein of treasure, struck upon but a few years back, is rapidly opened out by cunning explorers, until it leads to a mine of vast wealth, from which branch out in many directions new sources of power and might.

Among the branches of science in the practical applications of which the greatest strides have been made since the Association met at Leeds in 1858, is electricity. That year witnessed the accomplishment of the first great step towards the establishment of electrical communication between Europe and America, by the laying of a telegraph cable connecting Newfoundland with Valencia. Through this cable a message of thirty-one words was shortly afterwards transmitted in thirty-five minutes; an achievement which, though exciting great enthusiasm at the time, scarcely afforded promise of the succession of triumphs of ocean telegraphy which have since surpassed the wildest dreams of the pioneers in the realms of applied electricity.

The development of the electric telegraph constitutes a never-failing subject of the liveliest interest. The experiments made by Stephen Gray, in 1727, of transmitting electrical impulses through a wire 700 feet long; by Watson, twenty years afterwards, of transmitting frictional electricity through many thousand feet of wire, supported by a line of poles, on Shooter's Hill, in Kent; and by Franklin, who carried out a similar experiment at Philadelphia,—although they were followed by many other interesting and philosophical applications of frictional electricity to the transmission of signals—were not productive of really practical results. The work of Galvani and of Volta was more fruitful of an approach to practical telegraphy in the hands of Sömmering and of Coxe, while the researches of Oersted, of Ampère, of Sturgeon, and of Ohm, and especially the discoveries of volta-electric induction and magneto-electricity by Faraday, paved the way for the development of the electric telegraph as a practical reality by Cooke and Wheatstone in 1837. How remarkable the strides have been in the resources and powers of the telegraphist since that time is demonstrated by a few such facts as these; the first needle instrument of Cooke and Wheatstone transmitted messages at the rate of four words per minute, requiring five wires for that purpose; six messages are now conveyed by one single wire, at ten times that speed, and news is dispatched at the rate of 600 words per minute. Duplex working, which more than doubled the transmitting power of a submarine cable, was soon eclipsed by the application of Edison's quadruplex working, which has in its turn been surpassed by the multiplex system, whereby six messages may be sent independently, in either direction, on one wire. When last the British Association met in Leeds, submarine telegraphy had but just started into existence; thirty years later, the accomplished President of the Mechanical Section informed us, at our meeting at Bath, that 110,000 miles of cable had been laid by British ships, and that a fleet of nearly forty ships was occupied in various oceans in maintaining existing cables and laying new ones.

The important practical achievements by which most

formidable difficulties have been surmounted, step by step, in the successive attainment of the marvellous results of our day, have exerted an influence upon the advancement, not merely of electrical science, but also of science generally and of its applications, fully equal to that which they have exercised upon the development of commerce and of the intercourse between the nations of the earth.

Thus, the laying of the earliest submarine cables, between 1851 and 1855, led Sir W. Thomson, in conference with Sir George Stokes, to work out the theory of signalling in such cables, by utilising the mathematical results arrived at by Fourier in his investigation of the propagation of heat-waves. The failure of the first Atlantic cable led to the survey of the bottom of the Atlantic, which was the forerunner of deep-sea explorations, culminating in the work of the *Challenger Expedition*, and opening up new treasures of knowledge scarcely dreamt of when last the British Association met at Leeds. To the difficulties connected with the early attempts at submarine telegraphy, and the determination with which Thomson drove home the lessons learned, we owe the systematic investigations into the causes of the variations in resistance of copper conductors, and the consequent improvements in the metallurgy of copper, which led to the realisation of the high standard of purity of metal essential for the efficient working of telegraphic systems, and also to the extensive utilisation of electricity in the production of pure copper. The rare combination of originality in powers of research and perspicuity in mathematical reasoning, with inventive and constructive genius, for which Thomson has so long been pre-eminent, has placed at the disposal of the investigator of electric science, and of the practical electrician, instruments of measurement and record which have been of incalculable value, and which owe their origin to the theoretical conclusions arrived at by him in his researches into the conditions to be fulfilled for the attainment of practical success in the construction and employment of submarine cables. The mirror galvanometer, the quadrant electrometer, the syphon-recorder, and the divided-ring electrometer, are illustrations of the valuable outcome of Thomson's labours; the combination of the last-named instrument with sliding resistance coils has rendered possible the accurate sub-division of a potential difference into 10,000 equal parts. The general use of condensers in connection with cable signalling, due to Varley's application of them for signalling through submerged cables with induced short waves, was instrumental in establishing the fact that all electro-static phenomena are simply the result of starting an electric current of known short duration round a closed circuit. The practical application of the Wheatstone Bridge led to numerous important mathematical investigations, and induced Clerk Maxwell to devise a new mode of applying determinants to the solution of the complicated electrical problems connected with networks of conductors. The necessity for the universal recognition of an electrical unit of resistance led to the establishment, in 1860, of the Electrical Standards Committee of the British Association, whose long succession of important annual reports was instrumental in most important developments of theoretical electricity, and, indeed, served to open up the whole science of electrical measurement. Matthiessen's important investigations of the electrical behaviour of metals and their alloys, and the preparation and properties of pure iron, were the outcome of the commercial demand for a practically useful standard of electrical resistance, while Latimer Clark's practical standard of electromotive force, the mercurous sulphate cell, became invaluable to the worker in pure electrical research. The unit of resistance established by the British Association Committee received, in 1866, most important scientific application at the hands of Joule, who, by measuring the rate of development of heat in a wire of known resistance by the passage of a known current, obtained a new value of the mechanical equivalent of heat. This value differed

by about 1·3 per cent from the most accurate results arrived at by his experiments on mechanical friction, a difference which eventually proved to be exactly the error in the British Association unit of resistance; so that the true value of the unit of resistance, or ohm, was determined by Joule fifteen years before this result was achieved by electricians. Clerk Maxwell's remarkable electro-magnetic theory of light was put to the test, through the aid of the British Association unit of resistance, by Thomson, in determining the ratio of electro-magnetic unit to the electro-static unit of quantity. Many other most interesting illustrations might be given of the invaluable aid afforded to purely scientific research by the practical results of the development of electrical science, and of the constant co-operation between the science student and the practical worker. No one could, more fitly than the late Sir William Siemens, have maintained, as he did in his admirable Address at our meeting in Southampton, in 1882, that we owe most of the rapid progress of recent times to the man of science who partly devotes his energies to the solution of practical problems, and to the practitioner who finds relaxation in the prosecution of purely scientific inquiries. Most assuredly, both these classes of the world's benefactors may with equal right lay claim to rank the name of Siemens among those whom they count most illustrious!

In that highly interesting and valuable Address, delivered little more than a year before his sudden untimely removal from among us, the numerous important subjects discussed by him included not a few which he had made peculiarly his own in the wide range embraced by his enviable power of combining scientific research with practical work. Prominent among these were the applications of electric energy to lighting and heating purposes, and to the transmission of power, to the future development of which his personal labours very greatly contributed.

Siemens referred to the passing of the first Electric Lighting Bill, in the year of his Presidency, as being designed to facilitate the establishment of electric installations in towns; but the anxiety of the Government of that day to protect the interests of the public through local authorities led to the assignment of such power to these over the property of lighting companies, that the utilisation of electric lighting was actually delayed for a time by those legislative measures. There can now be no doubt, however, that this delay has really been in the interests of intending suppliers and of users of the electric light, as having afforded time for the further development of practical details, connected with generation and distribution, which was vital to the attainment of a fair measure of initial success. The subsequent important modification of legislation on the subject of electric lighting, together with the practical realisation of comparatively economical methods of distribution, the establishment of fairly equitable arrangements between the public and the lighting companies, and the apportionment, so far as the metropolis is concerned, of distinct areas of operation to different competing companies, have combined to place electric lighting in this country at length upon some approach to a really sound footing, and to give the required impetus to its extensive development. Nine companies either are now, or will very shortly be, actually at work supplying, from central stations, districts of London comprising almost the entire western and north-western portions of the metropolis. As regards other parts of England, there are already twenty-seven lighting stations actually at work in different towns, besides others in course of establishment and many more projected. The town of Leeds has not failed to give serious attention to the subject of utilising the electric light, and, although no general scheme has yet been adopted, the electricians who now visit this town will rejoice to see many of its public buildings provided with efficient electric illumination.

While the prediction made by Siemens, eight years ago,

that electric lighting must take its place with us as a public illuminant, has thus been already, in a measure, fulfilled, important progress is being continuously made by the practical electrician in developing and perfecting the arrangements for the generation of the supply, its efficient distribution from centres, and its delivery to the consumer in a form in which it can be safely and conveniently dealt with and applied at an outlay which, even now, does not preclude a considerable section of the public from enjoying the decided advantages presented by electric lighting over illumination by coal-gas. Yet our recent progress in this direction, encouraging though it has been, is insignificant as compared with the strides made in the application of electric lighting in the United States, as may be gauged by the fact that, while in America the number of arc lamps in use, in April of this year, was 235,000, and of glow lamps about three millions, there are at present about one-tenth the number of the latter, and one-hundredth the number of arc lamps, in operation in England.

In some important directions we may, however, lay claim to rank foremost in the application of the electric light; thus, our large passenger ships and our war ships are provided with efficient electrical illumination; to the active operations of our Navy the electric light has become an indispensable adjunct; and our system of coast defence, by artillery and submarine mines, is equally dependent, for its thorough efficiency, upon the applications of electricity in connection with range-finding, with the arrangement and explosion of mines, and with the important auxiliary in attack and defence, the electric light, which, while so arranged, at the operating stations, as to be protected against destruction by artillery fire and difficult of detection by the enemy, is available at any moment for affording invaluable information and important assistance and protection.

Other important applications of the electric light, such as its use as a lighthouse illuminant, for the lighting of main roads in coal mines, where its value is being increasingly appreciated, and even for signalling purposes in mid-air, through the agency of captive balloons, are continually affording fresh demonstrations of the value of this particular branch of applied electric science.

At the Electrical Exhibition at Vienna in 1883, where, not long before the lamented death of Siemens, I had the honour of serving as one of his colleagues in the representation of British interests, the progress which had been made in the construction of electrical measuring instruments since the French Exhibition and the Electrical Congress, two years before, was very considerable. The advance in this direction has been enormous since that time; but although the practical result of Thomson's and of Carlew's important work has been to supply us with trustworthy electrical balances and voltmeters, while efficient instruments have also been made by other well-known practical electricians, we have still to attain results in all respects satisfactory in these indispensable adjuncts to the commercial supply and utilisation of electric energy.

In connection with this important subject the recent completion of the Board of Trade standardising laboratory, established for the purposes of arriving at and maintaining the true values of electrical units, and of securing accuracy and uniformity in the manufacture of instruments supplied by the trade for electrical measurements, may be referred to with much satisfaction as a practical illustration of official recognition of the firm root which the domestic and industrial utilisation of electric energy has taken in this country.

The achievements of the telephone were referred to by Siemens in glowing terms eight years ago; but the results then attained were but indications of the direction in which telephonic inter-communication was destined speedily to become one of the most indispensable of present applications of electricity to the purposes of daily life. Preece, in speaking at Bath, two years ago, of the

advances made in applied electricity, showed that the impediments to telephonic communication between great distances had been entirely overcome; and now, although considerably behind America and France in the use of the telephone, we are rapidly placing ourselves upon speaking terms with our friends throughout the United Kingdom. The operations of the National Telephone Company well illustrate our progress in telephonic inter-communication: that company has now 22,743 exchange lines, besides nearly 5000 private lines, its exchanges number 272, and its call-offices 526. The number of instruments under rental in England has now reached 99,000; but, important as this figure is compared to our use of the telephone a very few years ago, it sinks into insignificance by the side of the number of instruments under rental in America, which at the beginning of the present year had reached 222,430, being an increase of 16,675 over the number in 1889. Only thirteen years have elapsed since the telephone was first exhibited as a practically workable apparatus to members of the British Association at the Plymouth Meeting, and the number of instruments now at work throughout the world may be estimated as considerably exceeding a million.

The successful transmission of the electric current, and the power of control now exercised over the character which electrically-transmitted energy is made to assume, are not alone illustrated by the efficiency of the arrangements already developed for the supply of the electric light from central stations. Siemens dwelt upon this subject at Southampton with the ardent interest of one who had made its development one of the objects of his energetic labours in later years, and also with a prophet's prognostications of its future importance. In speaking of the electric current as having entered the lists in competition with compressed air, the hydraulic accumulator, and the quick-running rope driven by water-power, Siemens pointed out that no further loss of power was involved in the transformation of electrical into mechanical energy than is due to friction, and to the heating of the conducting wires by the resistance they oppose, and showed that this loss, calculated upon data arrived at by Dr. John Hopkinson and by himself, amounted at the outside to 38 per cent. of the total energy. Subsequent careful researches by the Brothers Hopkinson have demonstrated that the actual loss is now much less than it was computed at in 1885, as much as 87 per cent. of the total energy transmitted being realisable at a distance, provided there be no loss in the connecting leads used.

The Paris Electric Exhibition of 1881 already afforded interesting illustrations of the performance of a variety of work by power electrically transmitted, including a short line of railway constructed by the firm of Siemens, which was a further development of the successful result already attained in Berlin by Werner Siemens in the same direction, and was, in its turn, surpassed by the considerably longer line worked by Messrs. Siemens at the Vienna Exhibition two years later. Various short lines which have since then been established by the firm of Siemens are well known, and one of the latest public acts in the valuable life of Siemens was to assist at the opening of the electric tramway at Portrush, in the installation of which he took an active part, and where the idea, so firmly rooted in his mind from the date of his visit to the Falls of Niagara, in 1876, of utilising water-power for electrical transmission—a result first achieved on a small scale by Lord Armstrong—was more practically realised than had yet been the case. Since that time Ireland has witnessed a further application of electricity to traction purposes, and of water-power to the provision of the required energy, in the working of the Bessbrook and Newry tramway, while London at length possesses an electric railway, three miles in length, to be very shortly opened, which will connect the City with one of the southern suburbs through a tram subway, and, although including many sharp curves and steep gradients, will be capable of conveying one hundred passengers at a time, at speeds

varying from thirteen to twenty-four miles per hour. During the past year a regular service of tramcars has been successfully worked, through the agency of secondary batteries, upon part of one of the large tramways of North London, with results which bid fair to lead to an extensive development of this system of working. The application of electricity to traction purposes has, however, received far more important development in the United States; at the commencement of this year there were in operation in different States 200 electrical tram-roads, chiefly worked upon the Thomson-Houston and the Sprague systems, and having a collective length of 1641 miles, with 2346 motor-cars travelling thereon. Further extensions are being rapidly made; thus, one company alone has 39 additional roads, of a collective length of 385 miles, under construction, to be worked through the agency of storage batteries.

The idea cherished by Siemens, and enlarged upon by him in more than one interesting address, of utilising the power of Niagara, appears about to be realised, at any rate in part; as a large tract of land has been recently acquired, by a powerful American Association, about a mile distant from the Falls, with a view to the erection of mills for utilising the power, which it is also proposed to transmit to distant towns; and an International Commission, with Sir William Thomson at its head, and with Mascart, Turretini, Coleman Sellers, and Unwin as members, will carefully consider the problems involved in the execution of this grand scheme.

The application of electric traction to water traffic, first successfully demonstrated in 1883, is receiving gradual development, as illustrated by the considerable number of pleasure boats which may now be seen on the Upper Thames during the boating season, and in connection with which Professor George Forbes proposed, at our meeting last year, that stations for charging the requisite cells, through the agency of water-power, should be established at the many weirs along the river, so as to provide convenient electric coaling stations for the river pleasure fleet.

Electrically-transmitted energy was first applied in Germany to haulage work in mines by the firm of Siemens some years ago, and great progress has since been achieved herein on the Continent and in America. Comparatively little has been accomplished in this direction in England; but it is very interesting to note, on the present occasion, that the first successful practical application of electricity in this country to pumping and underground haulage work was made in 1887, in this neighbourhood, at the St. John's Colliery, at Nornanton, where an extensive installation, carried out by Mr. Immisch, so well known in connection with electric launches, is furnishing very satisfactory results in point of economy and efficiency. The gigantic installations existing for the same purposes in Nevada and California afford remarkable illustrations of the work to be accomplished in the future by electrically-transmitted energy.

Among the many subjects of importance studied by Joule with the originality and thoroughness characteristic of his work, was the application of voltaic electricity to the welding and fusion of metals. Thirty-four years ago he published a most suggestive paper on the subject, in which, after dealing with the difficulties attending the operation of welding, and of the interference of films of oxide, formed upon the highly heated iron surfaces, with the production of perfect welds either under the hammer or by the methods of pressure (of which he then predicted the application to large masses of forged iron), he refers to the possibility of applying the calorific agency of the electric current to the welding of metals, and describes an operation witnessed by him in the laboratory of his fellow labourer, Thomson, of fusing together a bundle of iron wires by transmitting through them, when embedded in charcoal, a powerful voltaic current. Joule afterwards succeeded in fusing together a number of iron wires with the current of a Daniell battery, and of welding together

wires of brass and steel, platinum and iron, &c. In discussing the question of the amount of zinc consumed in a battery for raising a given amount of iron to the temperature of fusion, he points out that the same object would probably be more economically attained by the use of a magneto-electric machine, which would allow the heat to be provided by the expenditure of mechanical force, developed in the first instance by the expenditure of heat; and he indicates the possibility of arranging machinery to produce electric currents which shall evolve one-tenth of the total heat due to the combustion of the coal used, so that 5000 grains of coal applied through that agency would suffice for the fusion of one pound of iron. The successful practical realisation of Joule's predictions in regard to the application of electric currents, thus developed, to the welding of iron and steel, and to analogous operations, through the agency of the efficient machines devised by Professor Elihu Thomson, was demonstrated to the members of the Association by Professor Ayrton at Bath two years ago, and was shown upon a larger scale to visitors at the Paris Exhibition last year, and recently to highly interested audiences in London by our late President, Sir Frederick Bramwell. The latter demonstrated that the production of iron-welds by means of the Thomson machines was accomplished nearly twice as rapidly as by expert craftsmen; the perfection of the welds being proved by the fact that the strength of bars broken by tensile strains at the welds themselves was about 92 per cent of the strength of the solid metal. At the Crewe Works Mr. Webb is successfully applying one of these machines to a variety of welding work. The rapidity with which masses of metal of various dimensions are raised in those machines to welding heat is quite under control; the heat is applied without the advent of any impurities, as from fuel, and the speed of execution of the welding operation reduces to a minimum the time during which the heated surfaces are liable to oxidise. With such practical advantages as these, this system of electric welding bids fair to receive many useful applications.

Another very simple system of electric welding, especially applicable to thin iron and steel sheets, hoops, &c., has been contemporaneously elaborated in Russia by Dr. Bernados, and is already being extensively used. The required heat at the surfaces to be welded is developed by connecting the metal with the negative pole of the dynamo machine, or of a battery of accumulators, the circuit being completed by applying a carbon electrode to the parts to be heated; the reducing power of the carbon is said to preserve the heated metal surfaces from oxidation during the very brief period of heating. This mode of operation appears to have been practised upon a small scale, some years ago, by Sir William Siemens, to whom we also owe the first attempt to practically apply electric energy to the smelting of metals.

In his address in 1882 he referred to some results attained with his small electrical furnace, and pointed out that, although electric energy could, obviously, not compete economically with the direct combustion of fuel for the production of ordinary degrees of heat, the electric furnace would probably receive advantageous application for the attainment of temperatures exceeding the limits (about 1800° C.) beyond which combustion was known to proceed very sluggishly. This prediction appears to have been already realised through the important labours of Messrs. Cowles, who some years ago attacked the subject of the application of electricity to the achievement of metallurgical operations with the characteristic vigour and fertility of resource of our Transatlantic brethren. After very promising preliminary experiments, they succeeded, in 1885, at Cleveland, Ohio, in maturing a method of operation for the production of aluminium-bronze, ferro-aluminium, and silicium-bronze, with results so satisfactory as to lead to the erection of extensive works at Lockport, N.Y., where three dynamo-machines, each supplying a current of about 3000 amperes, are worked by water-power, through the agency of turbines, each of 500

h.-p., eighteen electric furnaces being now in operation for the production of aluminium alloys. These achievements have led to the establishment of similar works in North Staffordshire, where a gigantic dynamo-machine has been erected, furnishing a current of 5000 amperes, with an E.M.F. of 50 to 60 volts. The arrangement of the electrodes in the furnaces, the preparation of the furnace-charges (consisting of mixtures of aluminium ore with charcoal and with the particular granulated metal with which the aluminium is to become alloyed at the moment of its elimination from the ore); the appliances for securing safety in dealing with the current from the huge dynamo-machine, and many other details connected with this new system of metallurgic work, possesses great interest. Various valuable copper and aluminium alloys are now produced by alloying copper itself with definite proportions of the copper alloy, very rich in aluminium, which is the product of the electric furnace. The rapid production in large quantities of ferro-aluminium—which presents the aluminium in a form suitable for addition in definite proportions to fluid cast iron and steel—is another useful outcome of the practical development of the electric furnace by Messrs. Cowles.

The electric process of producing aluminium alloys has, however, to compete commercially with their manufacture by adding to metals, or alloys, pure aluminium produced by processes based upon the method originally indicated by Oersted in 1824, successfully carried out by Wöhler three years later, and developed into a practical process by H. St. Claire Deville in 1854—namely, by eliminating aluminium from the double chloride of sodium and aluminium in the presence of a fluoride, through the agency of sodium. An analogous process, indicated in the first instance by H. Rose—namely, the corresponding action of sodium upon the mineral cryolite, a double fluoride of aluminium and sodium—has also been recently developed at Newcastle, where the first of these methods was applied, upon a somewhat considerable scale, in 1860, by Sir Lowthian Bell, but did not then become a commercial success, mainly owing to the costliness of the requisite sodium. As the cost of this metal chiefly determines the price of the aluminium, technical chemists have devoted their best energies to the perfection and simplification of methods for its production, and the success which has culminated in the admirable Castner process constitutes one of the most interesting of recent illustrations of the progress made in technical chemistry, consequent upon the happy blending of chemical with mechanical science, through the labours of the chemical engineer.

Those who, like myself remember how, between forty and fifty years ago, a few grains of sodium and potassium were treasured up by the chemist, and used with parsimonious care in an occasional lecture experiment, cannot tire of feasting their eyes on the stores of sodium-ingots to be seen at Oldbury as the results of a rapidly and dexterously executed series of chemical and mechanical operations.

The reduction which has been effected in the cost of production of aluminium through this and other processes, and which has certainly not yet reached its limit, can scarcely fail to lead to applications of the valuable chemical and physical properties of this metal so widespread as to render it as indispensable in industries and the purposes of daily life as those well-known metals which may be termed domestic, even although, and, indeed, for the very reason that, its association with many of these, in small proportion only, may suffice to enhance their valuable properties or to impart to them novel characteristics.

The Swedish metallurgist, Wittenström, appears to have been the first to observe that the addition of small quantities of aluminium to fused steel and malleable iron had the effect of rendering them more fluid, and, by thus facilitating the escape of entangled gases, of ensuring the production of sound castings without any prejudicial effect upon the quality of the metal. The excellence of the

so-called Mitis castings, produced in this way, appears thoroughly established, and the results of recent important experiments seem to be opening up a field for the extensive employment of aluminium in this direction, provided its cost becomes sufficiently reduced. The valuable scientific and practical experiments of W. J. Keep, James Riley, R. Hadfield, Stead, and other talented workers in this country and the United States, are rapidly extending our knowledge in regard to the real effects of aluminium upon steel, and their causes. Thus, it appears to be already established that the modifications in some of the physical properties of steel resulting from the addition of that metal, are not merely ascribable to its actual entrance into the composition of the steel, but are due, in part, to the de-oxidation by aluminium of some proportion of iron-oxide which exists distributed through the metal, and prejudicially affects its fluidity when melted. In the latter respect, therefore, the influence exerted by aluminium, when introduced in small proportions into malleable iron and steel, appears to be quite analogous to that of phosphorus, silicon, or lead when these are added in small proportions to copper and certain of its alloys, the de-oxidation of which, through the agency of those substances, results in the production of sound castings of increased strength and uniformity. It is only when present in small proportion in the finished steel, that aluminium increases the breaking strain and elastic limit of the product.

The influence of aluminium, when used in small proportion, upon the properties of grey and white cast iron, is also of considerable interest, especially its effect in promoting the production of sound castings, and of modifying the character of white iron in a similar manner to silicon, causing the carbon to be separated in the graphitic form; with this difference—that the carbon appears to be held in solution until the moment of setting of the liquid metal, when it is instantaneously liberated, with the result that the structure of the cast metal and distribution of the graphite are perfectly uniform throughout.

The probable beneficial connection of aluminium with the industries of iron and steel naturally directs attention to the great practical importance, in the same direction, which has already been acquired, and promises to be in increasing measure attained, by certain other metals which, for long periods succeeding their discovery, have either been only of purely scientific interest and importance, or have acquired practical value in regard to their positions in a few directions quite unconnected with metallurgy. Thus, great interest attaches to the influence of the metals manganese, chromium, and tungsten upon the physical properties of steel and iron.

The name of Mushet is most prominently associated with the history of manganese in its relations to iron and steel. Half-a-century ago David Mushet carried out very instructive experiments on the influence exerted upon the properties of steel by the presence of manganese; and to Robert Mushet we owe the invaluable experiments leading to his suggestion to use manganese in the production of steel by the Bessemer process, which at once smoothed the path to the marvellously rapid and extensive development of the applications of steel produced by that classic method, and subsequently by the open-hearth or Siemens-Martin process—a development which has recently received its crowning illustration in the completion of one of the grandest of existing triumphs of engineering science and constructive skill—the Forth Bridge.

Robert Hadfield has recently contributed importantly to our knowledge of the relations of manganese to iron. His systematic study of the subject has revealed some very remarkable variations in the physical properties of so-called manganese-steel, according to the proportions of manganese which it contains. Thus, while the existence in steel of proportions ranging from 0.1 up to about 2.75 per cent improves its length and malleability, it becomes brittle if that limit is exceeded, the extreme of

brittleness being obtained with between 4 and 5 per cent of manganese; if, however, the percentage is increased to not less than 7, and up to 20, alloys of remarkable strength and toughness are obtained. Castings of high manganese steel, such as wheel-tyres, combine remarkable hardness with toughness. Even if the proportion of manganese is as high as 20 per cent in a steel containing 2 per cent of carbon, it can be forged; whereas it is very difficult to forge a steel of ordinary composition containing as much as 2.75 per cent of carbon. Another remarkable peculiarity of the high manganese steel is its behaviour when quenched in water. Instead of the heated metal being hardened and rendered brittle by the sudden cooling, like carbon steel, its tensile strength and its toughness are increased; so that water-quenching is really a toughening process, as applied to the manganese alloy; and an interesting feature connected with this is that, the colder the bath into which the highly-heated metal is plunged, the tougher is the product. The curious effect of manganese in reducing, and even destroying, the magnetic properties of iron was already noticed by Rinman nearly 120 years ago; one result of Hadfield's important labours has been to place in the hands of such eminent physicists as Thomson, John Hopkinson, and Reinold, materials for the attainment of most interesting information respecting the electrical and other physical characteristics of manganese steel. Hopkinson, from experiments with a sample of steel containing 12 per cent of manganese, estimated that not more than 9 out of the 86 per cent of the iron composing the mass was magnetic, and he considered that the manganese enters into that which must, for magnetic purposes, be regarded as the molecule of iron, completely changing its properties, a fact which must have great significance in any theory regarding the nature of magnetisation. The great hardness of manganese steel, and the consequent difficulty of dealing with it by means of cutting-tools, constitute at present the chief impediments to its technical applications in many directions; but where great accuracy of dimensions is not required, and where great strength is an essential, it is already put to valuable uses.

The importance of manganese in connection with the metallurgy of iron and steel is in a fair way of finding its rival in that of the metal chromium, the employment of which, as an alloy with steel, was first made the subject of experiment in 1821, by Berthier, who was led by the important experiments of Faraday and Stoddart, then just published, to endeavour to alloy chromium with steel, and obtained good results by fusing steel together with a rich alloy of chromium and iron, so as to introduce about 15 per cent of the former into the metal. Further small experiments were made the year following, by Faraday and Stoddart, in the same direction; but chrome steel appears to have been first produced commercially at Brooklyn, N.Y., sixteen years ago. Ten years later its manufacture had become developed in France, and the varieties of chrome steel produced in the Loire district now receive important and continually extending applications, on account of their combining comparative hardness with high tenacity, and only little loss in ductility, and of their acquiring great closeness of structure when tempered.

The influence of chromium upon the character of steel differs in several marked respects from that exercised by manganese; thus, chrome steels weld badly, or not at all, whereas manganese steels weld very readily, and work under the hammer better than ordinary carbon steel. Again, the remarkable influence of manganese upon the magnetic properties of steel and iron is not shared by chromium. Chrome steel has for some time been a formidable rival of the very highest qualities of carbon steel produced for cutting tools, and of the valuable tungsten steel which we owe to Robert Mushet. The great hardness, high tenacity, and exceeding closeness of structure possessed by suitably tempered steel containing hot more than from 1 to 1.5 per cent of chromium, and

from 0.8 to 1 per cent of carbon, renders this material invaluable for war purposes: cast projectiles, when suitably tempered, have penetrated compound steel and iron plates over 9 inches in thickness, such as are used upon armoured ships of war, without even sustaining any important change of form. The proper tempering of these projectiles necessitates their being produced hollow; their cavities or chambers are only of small capacity, but the charge of violent explosive which they can contain, and which can be set into action without the intervention of fuse or detonating appliance, suffices to tear these formidable punching tools into fragments as they force their way irresistibly through the armoured side of a ship, and to violently project those fragments in all directions, with fearfully destructive effects. The employment of chromium as a constituent of steel plates used for the protection of ships of war is already being entered upon, and the influence exerted by the presence of that metal in small quantities in steel employed in the construction of guns is also at present a subject of investigation. At Crewe, Mr. F. Webb has for some time past used chromium, with considerable advantage, in the production of high-quality steels for railway requirements.

The practical results attained by the introduction of copper and of nickel as components of steel have also recently attracted much attention. At the celebrated French Steel Works of M. Schneider, at Creuzot, the addition of a small percentage of copper to steel used for armour plates and projectiles is practised, with the object of imparting hardness to the metal without prejudice to its toughness. James Riley has found that the presence of aluminium in very small quantities facilitates the union of steel with a small proportion of copper, and that the latter increases the strength but does not improve the working qualities of steel. With nickel, Riley has obtained products analogous in many important respects to manganese steel; the remarkable differences in the physical properties of the manganese alloys, according to their richness in that metal, are also shared by the nickel alloys, some of these being possessed of very valuable properties; thus, it has been shown by Riley that a particular variety of nickel-steel presents to the engineer the means of nearly doubling boiler-pressures, without increasing weight or dimensions. He has, moreover, found the co-existence of manganese in small quantity with nickel in the alloy to contribute importantly to the development of valuable physical properties.

The careful study of the alloys of aluminium, chromium, manganese, tungsten, copper, and nickel, with iron and with steel, so far as it has been carried, with especial reference to the influence which they respectively exercise upon the salient physical properties of those materials, even when present in them in only very small proportions, has demonstrated the importance of a more searching or complete application of chemical analysis, than hitherto practised, to the determination of the composition of the varieties of steel which practical experience has shown to be peculiarly adapted to particular uses. It appears, indeed, not improbable that certain properties of these, which have been ascribed to slight variations in the proportion or the condition of the constituent carbon, or in the amounts of silicium, phosphorus, and manganese which they contain, may sometimes have been due to the presence in minute quantities of one or other of such metals as those named, and to the effects which they produce, either directly, or indirectly by modifying or counteracting the effects of the normal constituents of steel. The important part now played by manganese in steel manufacture is an illustration of the comparatively recent results of research, and of practical work based on research, in these directions, and the effects of the presence in steel of only very small quantities of some of the other metals named are already, as I have pointed out, being similarly understood and utilised.

Such systematic researches as those upon which

Osmond, Roberts-Austen, and many other workers have been for some time past engaged, may make us acquainted with the laws which govern the modifications effected in the physical characteristics of metals by alloying these with small proportions of other metals. The suggestion of Roberts-Austen that such modifications may have direct connection with the periodic law of Mendeleeff, which may furnish explanations of the causes of specific variations in the properties of iron and steel, has been followed up energetically by Osmond, who has experimentally investigated the thermal influence upon iron of the elements phosphorus, sulphur, arsenic, boron, silicon, nickel, manganese, chromium, copper, and tungsten. He regards his results as being quite confirmatory of the soundness of Roberts-Austen's suggestion, as they demonstrate that foreign elements having atomic volumes lower than iron tend to make it assume or preserve the particular molecular form in which it has itself the lowest atomic volume, while the converse is the case for the foreign elements of high atomic volume. An analogous influence was found to be exerted by those two groups of elements upon the permanent magnetisation of steel.

Captivating as such deductions are, those who have devoted much attention to the practical investigation of iron, steel, and other metals, cannot but feel that much caution has to be exercised in drawing broad conclusions from the results of such researches as these. Like the investigations recently made with the object of ascertaining the condition in which carbon exists in steel, and the part played by it in determining the modifications in the properties developed in that material by the influence of temperature and of work done upon it, they are surrounded by formidable difficulties, arising from the practical impossibility of altogether eliminating the disturbing influences of minute quantities of foreign elementary bodies, co-existing in the metal operated upon, with those whose effects we desire to study. Certain it is, however, that by acquiring an accurate acquaintance with the composition of varieties of iron and steel exhibiting characteristic properties; by preserving in the all-important work of systematic practical examination of the mechanical and physical peculiarities developed in iron and steel of known composition by their association with one or more of the rarer metals in varied proportions, and by the further prosecution of chemical and physical research in such directions as those which have already been fruitful of most instructive results, such talented labourers as Chernoff, Osmond, Roberts-Austen, Barus and Stroudal, Hadfield, Keepe, James Riley, Stead, Turner, and others, cannot fail to contribute continually to the development of improvements equalling in importance those already attained in the production, treatment, and methods of applying cast iron, malleable iron, and steel, or alloys equivalent to steel in their qualities.

The causes of the variations in the physical properties of steel produced by the so-called hardening, annealing, and tempering processes were for very many years a fruitful subject for experimental inquiry, as well as of theoretical speculation with regard to the condition in which the carbon is distributed in steel, according to whether the metal is hardened or annealed, or in an intermediate, tempered state. Recent researches have made our knowledge in the latter direction fairly precise; as yet, however, we are only on the track of definite information respecting the nature and extent of connection between the physical peculiarities of steel in those different conditions and the established differences in the form and manner in which the carbon is disseminated through it.

The careful systematic study of the modifications developed in certain physical properties of iron and steel by gradual changes of temperature between fusion of the metal and the normal temperature, has shown those modifications to be governed by a constant law, and that at certain critical temperatures special phenomena present

themselves. This important subject, which was so clearly brought before the Association last year in the interesting lecture of Roberts-Austen, has been and is still being pursued by accomplished workers, among whom the most prominent is F. Osmond. The phenomenon of recalcence, or the re-glowing of, or liberation of heat in, iron and steel at certain stages during the cooling process, first noticed by Gore, and examined into by Barrett, appears to be the result of actual chemical combination between the metal and its contained carbon at the particular temperature attained at the time; while the absorption of heat, demonstrated by the arrest in rise of temperature during its continuous application to the metal, is ascribed to the elimination, within the mass, of carbon as an iron carbide perfectly stable at low temperatures. The pursuit of a well-devised system of experimental inquiry into this subject has led Osmond to propound theories of the hardening and tempering of steel, which are at present receiving the careful study of physicists and chemists, and cannot fail to lead to further important advancement of our knowledge of the true nature of the influence of carbon upon the properties of iron.

Another important subject connected with the treatment of masses of steel, and with the influence exercised upon their physical characteristics by the processes of hardening and tempering, and by submitting them to oft-repeated concussion or vibrations, or frequent or long-continued strains, is the development and maintenance, or gradual disappearance, of internal stresses in the masses—one of the many important subjects to which attention was directed by Dr. Anderson, the Director-General of Ordnance Factories, in his very suggestive address to the Mechanical Section last year. This question is one of especial interest to the constructor of steel guns, as the powers of endurance of these do not simply depend upon the quality of the material composing them, but are very largely influenced by the treatment which it receives at the hands of the gunmaker. Indeed, the highest importance attaches to the processes which are applied to the preliminary preparation of the individual parts of which the gun is constructed, and to the putting together of these so as to ensure their being and remaining in the physical condition best calculated to assist each other in securing for the structure the power of so successfully resisting the heavy strains to which it has to be subjected, as to suffer little alteration other than that due to the superficial action of the highly-heated products of explosion of the charges fired in the gun. The development of internal strains in objects of steel, especially by the hardening and tempering processes, or by their exposure to conditions favourable to unequal cooling of different parts of the mass, has long been a subject of much trouble and of experimental inquiry in connection with many applications of steel. Systematic experiments of the kind commenced, about eighteen years ago, by the late Russian general, Kalakoutsky, are now being pursued at Woolwich, with the objects of determining the nature and causes of internal stresses in steel gun-hoops and tubes, and in shells, and of thereby establishing the proper course to be adopted for avoiding, lessening, or counteracting injurious stresses, on the one hand, and for setting up stresses beneficial to the powers of endurance of guns on the other. One method of experiment pursued, with parts of guns, is to cut narrow hoops off the forgings, after a particular treatment, which are then cut right across at one place, it being observed whether, and to what extent, the resulting gaps open or close. This important subject has also been similarly investigated by my talented old friend and fellow worker, the President this year of the Mechanical Section, Captain Andrew Noble, whose name in connection with the science and practice of artillery is familiar to us as household words.

(To be continued).

ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.

By Professor T. E. THORPE, B.Sc., Ph.D., F.R.S., Treas.C.S.,
President of the Section.

LEEDS has one most notable association with chemistry of which she is justly proud. In the month of September, 1767, Dr. Joseph Priestley took up his abode in this town. The son of a Yorkshire cloth-dresser, he was born in 1733 at Fieldhead, a village about six miles hence. His relatives, who were strict Calvinists, on discovering his fondness for books, sent him to the Academy at Daventry to be trained for the ministry. In spite of his poverty and of certain natural disadvantages of speech and manner, he gradually acquired, more especially by his controversial and theological writings, a considerable influence in Dissenting circles. A pressing invitation and the offer of one hundred guineas a year, induced him to accept an invitation to take charge of the congregation of Mill Hill Chapel here. He was already known to science by his "History of Electricity," and the effort was made to attach him still more closely to its cause by the offer of an appointment as naturalist to Cook's Second Expedition to the South Seas. But thanks to the intervention of some worthy ecclesiastics on the Board of Longitude who had the direction of the business, and who, as Professor Huxley once put it, "possibly feared that a Socinian might undermine that piety which in the days of Commodore Truncheon so strikingly characterised sailors," he was allowed to remain in Leeds, where, as he tells us in his Memoirs, he continued six years, "very happy with a liberal, friendly, and harmonious congregation," to whom his services (of which he was not sparing) were very acceptable. "In Leeds," he says, "I had no unreasonable prejudices to contend with, and I had full scope for every kind of exertion."*

We have every reason to feel grateful to the "worthy ecclesiastics," since their action indirectly occasioned Priestley to turn his attention to chemistry. The accident of living near a brewery led him to study the properties of "fixed air," or carbonic acid, which is abundantly formed in the process of fermentation, and which at that time was the only gas whose separate and independent existence had been definitely established. From this happy accident sprang that extraordinary succession of discoveries which earned for their author the title of the Father of Pneumatic Chemistry, and which were destined to completely change the aspect of chemical theory and to give it a new and unexpected development.

I have been led to make this allusion to Priestley, not so much on account of his connection with this place as for the reason that, as it seems to me, there has been a disposition to obscure his true relation to the marvellous development of chemical science which made the close of the last century memorable in the history of learning. Our distinguished fellow-worker, M. Berthelot, the Perpetual Secretary of the French Academy, has recently published, under the title of "La Révolution Chimique," a remarkable book, written with great skill, and with all the charm of style and perspicacity which invariably characterises his work, in which he claims for Lavoisier a participation in discoveries which we count among the chief scientific glories of this country. From the eminence of M. Berthelot's position in the world of science, his book is certain to receive in his own country the attention which it merits, and as it is issued as one of the volumes of the Bibliothèque Scientifique Internationale it will probably obtain through the medium of translations a still wider circulation. I trust that I shall not be accused of being unduly actuated by what Mr. Herbert

Spencer terms "the bias of patriotism" in deeming the present a fitting occasion on which to bring these claims to your notice with a view of determining how far they can be substantiated.

All who are in the least degree familiar with the history of chemical science during the last hundred years will recognise, as I proceed, that the claims which M. Berthelot asserts on behalf of his illustrious predecessor are not put forward for the first time. Explicitly made, in fact by Lavoisier himself, they were uniformly and consistently disallowed by his contemporaries. M. Berthelot now seeks to support them by additional evidence, and to strengthen them with new arguments, and asks us thereby to clear the memory of Lavoisier from certain grave charges which lie heavily on it. You have doubtless anticipated that these claims have reference to Lavoisier's position in relation to the discovery of oxygen gas and the determination of the non-elementary nature of water.

The substance we now call oxygen—a name we owe to Lavoisier—was discovered by Priestley on August 1, 1774; he obtained it, as every schoolboy knows, by the action of heat upon the red oxide of mercury. We all remember the characteristically ingenuous account which Priestley gives of the origin of his discovery. M. Berthelot sees in it merely the evidence of the essentially empirical character of his work. "Priestley," he says, "the enemy of all theory and of every hypothesis, draws no general conclusion from his beautiful discoveries, which he is pleased, moreover, not without affectation, to attribute to chance. He describes them in the current phraseology of the period with an admixture of peculiar and incoherent ideas, and he remained obstinately attached to the theory of phlogiston up to his death, which occurred in 1804" (p. 40). Such a statement is calculated to give an erroneous idea of Priestley's merit as a philosopher. That the implication it contains is wholly opposed to the real spirit of his work might be readily shown by numerous quotations from his writings. Perhaps this will suffice. "It is always our endeavour, after making experiments, to generalise the conclusions we draw from them, and by this means to form a *theory* or system of principles to which all the *facts* may be reduced, and by means of which we may be able to foretell the result of future experiments." This quotation is taken from the concluding chapter of his "Experiments and Observations on Different Kinds of Air," in which he actually seeks to draw "general conclusions" concerning the constituent principles of the various gases which he himself made known to us, and to show the bearing of these conclusions on the doctrine of phlogiston. That he was content to rest in the faith of Stahl's great generalisation, even to the end, is true, and the fact is the more remarkable when we recall the absolute sincerity of the man, his extraordinary receptivity, and, as he says of himself, his proneness "to embrace what is generally called the heterodox side of almost every question." If it is argued that this merely shows Priestley's inability to appreciate theory, it must be at least admitted that there is no proof that he was inimical to it. His position is clearly evident from the concluding words of the section of his work from which I have already quoted. "This doctrine of the composition and decomposition of water has been made the basis of an entirely new system of chemistry, and a new set of terms has been invented and appropriated to it. It must be acknowledged that substances possessed of very different properties may, as I have said, be composed of the same elements in different proportions and different modes of combination. It cannot, therefore, be said to be absolutely impossible but that water may be composed of these two elements or any other. But then the supposition should not be admitted without *proof*, and if a former theory will sufficiently account for all the *facts* there is no occasion to have recourse to a new one, attended with no peculiar advantage (*loc. cit.*, p. 543).

I should not feel much reluctance to adopt the *new doctrine*, provided any new and stronger evidence be

* Leeds still enjoys one of the fruits of Priestley's insatiable power of work in her admirable Proprietary Library. He seems to have suggested its formation and was its first honorary secretary.

produced for it. But though I have given all the attention that I can to the experiments of M. Lavoisier, &c., I think that they admit of the easiest explanation on the old system" (*loc. cit.*, p. 563).

The fact that Priestley was the first to consciously isolate oxygen is not contested by M. Berthelot, although he is careful to point out, what is not denied, that the exact date of the discovery depends on Priestley's own statement, and that his first publication of it was made in a work published in London in 1775. It was known before Priestley's famous experiment that the red oxide of mercury, originally formed by heating the metal in contact with air, would again yield mercury by the simple action of heat and without the intervention of any reducing agent. Bayen, six months before the date of Priestley's discovery, had observed that a gas was thus disengaged, but he gave no description of its nature, contenting himself merely by pointing out the analogy which his experiments appeared to possess to those of Lavoisier on the existence of an elastic fluid in certain substances. Afterwards, when the facts were established, Bayen drew attention to his earlier experiments and claimed, not only the discovery of oxygen, but all that Lavoisier deduced from it. "But," says M. Berthelot, in reference to this circumstance, "his contemporaries paid little heed to his pretensions, nor will posterity pay more" ("La Révolution Chimique," p. 60).

M. Berthelot, however, does not dismiss Lavoisier's claims to a participation in the discovery in the same summary fashion. On the contrary, whilst not explicitly claiming for him the actual isolation, in the first instance, of oxygen, the whole tenor of his argument is to extenuate, and even to justify, his demand to be regarded as an independent discoverer of the gas. He begins by asserting that Lavoisier had already a presentiment of its existence in 1774, and he quotes, in support of this assumption, an abstract from Lavoisier's memoir, published in December, 1774, in the *Journal de Physique* of the Abbé Rozier. "This air, deprived of its fixable portion (by metals during calcination), is in some fashion decomposed, and this experiment would seem to afford a method of analysing the fluid which constitutes our atmosphere and of examining the principles of which it is composed. . . . I believe I am in a position to affirm that the air, as pure as it is possible to suppose it, free from moisture and from every foreign substance, far from being a simple body, or element, as is commonly thought, should be placed, on the contrary, . . . in the group of the mixtures, and perhaps even in that of the compounds."

M. Berthelot further asserts that Lavoisier was at this time the first to recognise the true character of air, and he expresses his belief that it is probable that he would himself have succeeded in isolating its constituents if the path of inquiry had been left to him alone. It is no disparagement to Lavoisier's prescience to say that there is nothing in these lines, nor in the memoir of the repetition of Boyle's experiments on the calcination of tin to which they refer, to show that Lavoisier had made any advance beyond the position of Hooke and Mayow. It has been more than once pointed out that the chemists of the seventeenth century understood the true nature of combustion in air much better than their brethren of the last quarter of the eighteenth century. Hooke, in the *Micrographia*, and Mayow, in his "Opera Omnia Medico-physica," indicated that combustion consists in the union of something with the body which is being burnt; and Mayow, both by experiment and inference, demonstrated in the clearest way the analogy between respiration and combustion, and showed that in both processes one constituent only of the air is concerned. He distinctly stated that, not only is there increase of weight attending the calcination of metals, but that this increase is due to the absorption of the same *spiritus* from the air that is necessary to respiration and combustion. Mayow's experiments are so precise, and his facts so incontestable, that, as Chevreul has said, it is surprising that the truth

was not fully recognised until a century after his researches (*Vide* Watts' "Dictionary of Chemistry," by Morley and Muir, art. "Combustion," p. 242).

It is now necessary to examine Lavoisier's claims rather more closely and in the light of M. Berthelot's book. A *résumé* of his work "On the Calcination of Tin" was given by Lavoisier to the Academy in November, 1774, but the complete memoir was not deposited until May, 1777. A careful comparison of an abstract of what was stated to the Academy in November, 1774, contributed by Lavoisier himself, in December, 1774, to the *Journal de Physique* of the Abbé Rozier, makes it evident that very substantial additions were made to the communication before it was finally printed in the *Mémoires de l'Académie des Sciences*. The possibility of this is allowed by M. Berthelot. He says (p. 58):—"A summary communication, often given *vis à vis* to a learned society, such as the Academy of Sciences of Paris or the Royal Society of London, would immediately call forth verifications, ideas, and new experiments, which would develop the range and even the results of such communication. The original author, when printing his memoir, would in return—and for this he is hardly blamable—embody these additional results and later interpretations. It thus becomes most difficult to assign impartially to each his share in a rapid succession of discoveries" (*Loc. cit.*, p. 58).

But although, as we shall see, Lavoisier was certainly aware of Priestley's great discovery, no allusion is made to the gas, nor to Priestley's previous work on the other constituent of air, which is printed in the *Philosophical Transactions* for 1772, and for which he was awarded the Copley Medal by the Royal Society. It is simply impossible to believe that Lavoisier could have been influenced by this work. Indeed, we venture to assert that the full and clear recognition of the non-elementary nature of air which he eventually made was based upon it. It is noteworthy that in the early part of his memoir he states his opinion that the addition, not only of powdered charcoal, but of any phlogistic substance to a metallic calx is attended with the formation of fixed air. It is certain that at this period he had, not only not consciously obtained any gas resembling Priestley's dephlogisticated air from any calx with which he had experimented, but that none of his experiments had afforded him any idea that the gas absorbed during calcination was identical with it.

At Easter, 1775, Lavoisier presented a memoir to the Academy "On the Nature of the Principle which Combines with Metals during Calcination." This was "*reçu le 8 Août, 1778*." To the memoir there is a note stating that the first experiments detailed in it were performed more than a year before; those on the red precipitate were made by means of a *burning glass* in the month of November, 1774, and were repeated in the spring of 1775 at Montigny in conjunction with M. Trudaine. In this paper Lavoisier first distinctly announces that the principle which unites with metals during their calcination, which increases their weight, and which transforms them into calces, is nothing else "than the purest and most salubrious part of the air; so that if that air which has been fixed in a metallic combination again becomes free, it re-appears in a condition in which it is eminently respirable, and better adapted than the air of the atmosphere to support inflammation and the combustion of substances" ("Œuvres de Lavoisier," official edition, vol. ii., p. 123). He then describes the method of preparing oxygen by heating the red oxide of mercury, and compares its properties with those of fixed air. There is, however, no mention of Priestley, nor any reference to his experiments. It can hardly be doubted that in this memoir Lavoisier intended his readers to believe that he was "the true and first discoverer" of the gas which he afterwards named oxygen. This is borne out by certain passages in his subsequent memoir "On the Existence of Air in Nitrous

Acid; *lu le 20 avril, 1776, remis en décembre 1777.*" He had occasion incidentally to prepare the red oxide of mercury by calcining the nitrate, and says that he obtained from it a large quantity of an air "much purer than common air, in which candles burnt with a much larger, broader, and more brilliant flame, and which in no one of its properties differed from that which I had obtained from the calx of mercury, known as *mercurius precipitatus per se*, and which Mr. Priestley had procured from a great number of substances by treating them with nitric acid."

In another part of this memoir he says that "perhaps, strictly speaking, there is nothing in it of which Mr. Priestley would not be able to claim the original idea; but as the same facts have conducted us to diametrically opposite results, I trust that, if I am reproached for having borrowed my proofs from the works of this celebrated philosopher, my right at least to the conclusions will not be contested." M. Berthelot remarks on the irony of this passage: we may infer from it that the friends of the English chemist had not been altogether idle. In his memoir "On the Respiration of Animals," read to the Academy in 1777, he again appears to admit the claim of Priestley to at least a share in the discovery. "It is known from Mr. Priestley's and my experiments that *mercurius precipitatus per se* is nothing but a combination," &c. In several subsequent communications Priestley's name is mentioned in very much the same connection, until we come to the classical memoir "On the Nature of the Acids," when it is said:—"I shall henceforth designate the dephlogisticated air, or the eminently respirable air . . . by the name of the *acidifying principle*, or, if it is preferred to have the same signification under a Greek word, by that of the "*principe oxygene*."

In none of the memoirs after that of Easter 1775 is the claim for participation more than implied; it is made explicitly for the first time in the paper "On a Method of Increasing the Action of Fire," printed in the *Mémoires de l'Académie* for 1782, and in these words:—"It will be remembered that at the meeting of Easter 1775, I announced the discovery, which I had made some months before with M. Trudaine,* in the laboratory of Montigny, of a new kind of air, up to then absolutely unknown, and which we obtained by the reduction of *mercurius precipitatus per se*. This air, which Mr. Priestley discovered at very nearly the same time as I, and I believe even before me, and which he had procured mainly from the combination of minium and of several other substances with nitric acid, has been named by him *dephlogisticated air*."

In the "Traité Élémentaire de Chimie" the claim for participation is again asserted in these words:—"This air, which Mr. Priestley, Mr. Scheele, and I discovered at about the same time . . ."

Now there is no question that Lavoisier knew of the existence of oxygen some months before he made the experiments with the burning glass of M. Trudaine at Montigny for the simple reason that Priestley had already told him of it. Priestley left Leeds in 1773, to become the librarian and literary companion of Lord Shelburne, and in the autumn of 1774 he accompanied his lordship on to the Continent, and spent the month of October in Paris. Lavoisier was famous for his hospitality; his dinners were celebrated; and Priestley, in common with every foreign *savant* of note who visited Paris at that period, was a welcome guest. What followed is best told in Priestley's own words. "Having made the discovery [of oxygen] some time before I was in Paris, in the year 1774, I mentioned it at the table of Mr. Lavoisier, when most of the philosophical people of the city were present, saying that it was a kind of air in which a candle burnt much better than in common air, but I had not then given it any name. At this all the company, and Mr. and Mrs. Lavoisier as much as any, expressed great surprise. I

told them I had gotten it from *precipitate per se* and also from red lead. Speaking French very imperfectly, and being little acquainted with the terms of chemistry, I said *plombe rouge*, which was not understood until Mr. Macquer said I must mean minium."

In his account of his own work on dephlogisticated air, given in his "Observations," &c., 1790 edition, he further says (vol. ii., p. 108):—"Being at Paris in the October following [the August of 1774], and knowing that there were several very eminent chemists in that place, I did not omit the opportunity, by means of my friend Mr. Magellan,* to get an ounce of *mercurius calcinatus* prepared by Mr. Cadet, of the genuineness of which there could not possibly be any suspicion; and, at the same time, I frequently mentioned my surprise at the kind of air which I had got from this preparation to Mr. Lavoisier, Mr. le Roy, and several other philosophers, who honoured me with their notice in that city, and who, I dare say, cannot fail to recollect the circumstance."

If any further evidence is required to prove that Lavoisier was not only not "the true and first discoverer" of oxygen, but that he has absolutely no claim to be regarded even as a later and independent discoverer, it is supplied by M. Berthelot himself. Not the least valuable portion of M. Berthelot's book, as an historical work, is that which he devotes to the analysis of the thirteen laboratory journals of Lavoisier, which have been deposited, by the pious care of M. de Chazelles, his heir, in the archives of the Institute. M. Berthelot has given us a synopsis of the contents of almost every page of these journals, with explanatory remarks and dates when these could be ascertained. As he well says, these journals "are of great interest because they inform us of Lavoisier's methods of work and of the direction of his mind—I mean the successive steps in the evolution of his private thought." On the fly-leaf of the third journal is written, "*du 23 mars, 1774, au 13 février, 1776.*" From p. 30 we glean that Lavoisier visited his friend M. Trudaine at Montigny about ten days after his conversation with Priestley, and repeated the latter's experiments on the marine acid and alkaline airs (hydrochloric acid gas and ammonia). He is again at Montigny some time between the February 28 and the March 31, 1775, and repeats, not only Priestley's experiments on the decomposition of mercuric oxide, presumably by means of M. Trudaine's famous burning glass, but also his observations on the character of the gas. The fly-leaf of the fourth journal informs us that it extends from February 13, 1776, to March 3, 1778. On p. 1 is an account of experiments made February 13 on "*précipité per se* chez M. Baumé, in which the disengaged gas is spoken of as "*l'air déphlogistique de M. Priestley*" (*sic*). Such a phrase in a private note-book is absolutely inconsistent with the idea that at this time Lavoisier considered himself as an independent discoverer of the gas. How he came to regard himself as such we need not enquire. Nor is it necessary to occupy your time by any examination of the arguments by which M. Berthelot, with the skill of a practised advocate, would seem to identify himself with the case of his client. We would do him the justice of recognising the difficulty of his position. He seeks to discharge an obligation, of which the acknowledgment has been too long delayed. The Académie des Sciences a year ago awoke to the sense of its debt of gratitude to the memory of the man who had laboured so zealously for its honour and even for its existence, during the stormy period of which France has just celebrated the centenary, and out of the *éloge* on Lavoisier which M. Berthelot, as Perpetual Secretary, was commissioned to deliver, has grown La Révolution Chimique. To write eulogy, however, is not necessarily to write history. We

* Prof. Grimaux (Lavoisier, p. 51), says: "Un de ses [Lavoisier's] amis qui habitait Londres, Magalhaens ou Magellan, de la famille du célèbre navigateur, lui en voyait tous les mémoires sur les sciences qui paraissaient en Angleterre et le tenait au courant des découvertes de Priestley."

* M. Trudaine de Montigny died in 1777.

cannot but think that M. Berthelot has been hampered by his position, and that his opinion, or at least the free expression of it, has been fettered by the conditions under which he has written. We imagine we discern between the lines the consciousness that, to use Brougham's phrase, the brightness of the illustrious career which he eulogises is dimmed with spots which a regard for historical truth will not permit him wholly to ignore.

Two cardinal facts made the downfall of phlogiston complete—the discovery of oxygen and the determination of the compound nature of water. M. Berthelot's contention is that, not only did Lavoisier effect the overthrow, but he also discovered the facts. In other words, he has, not only a claim to a participation in the discovery of oxygen, but he is also "the true and first discoverer" of the non-elementary nature of water. This second claim is directly and explicitly stated. Although it is supported by a certain ingenuity of argument, we venture to think that we shall be able to show that it has no greater foundation in reality than the first.

Members of the British Association, who are at all familiar with its history, will recall the fact that this is not the first occasion on which the attempt to transfer "those laurels which both time and truth have fixed upon the brow of Cavendish" has had to be resisted. At the Birmingham Meeting of 1839 the Rev. W. Vernon Harcourt, who then presided, devoted a large portion of his Address to an able and eloquent vindication of Cavendish's rights. The attack came then as now from the Perpetual Secretary of the French Academy, and the charges were also formulated then, as now, in an *éloge* read before that learned body. The assailant was M. Arago, who did battle, not for his countryman Lavoisier, whose claims are dismissed as "pretensions," but on behalf of James Watt, the great engineer, who was one of the foreign members of the Institute.

It is not my wish to trouble you at any length with the details of what has come to be known in the history of scientific discovery as the Water Controversy—a controversy which has exercised the minds and pens of Harcourt, Whewell, Peacock, and Brougham in England; of Brewster, Jeffrey, Muirhead, and Wilson in Scotland; of Kopp in Germany; and of Arago and Dumas in France. This controversy, it has been said, takes its place in the history of science side by side with the discussion between Newton and Leibnitz concerning the invention of the Differential Calculus, and that between the friends of Adams and Leverrier in reference to the discovery of the planet Neptune. Up to now it has practically turned upon the relative merits of Cavendish and Watt. M. Berthelot is the first French *savant* of any note who has seriously put forward the claims of Lavoisier, his countryman and predecessor Dumas having deliberately rejected them.

At the risk of wearying you with detail, I am under the necessity of re-stating the facts in order to make the position clear. Some time before April 18, 1781, Priestley made what he called "a random experiment" for the entertainment of a few philosophical friends. It consisted in exploding a mixture of inflammable air (presumably hydrogen) and common air, contained in a closed glass vessel, by the electric spark, in the manner first practised by Volta in 1776. The experiment was witnessed by Mr. John Warltire, a lecturer on natural philosophy and a friend of Priestley, who had rendered him the signal service of giving him the sample of the mercuric oxide from which he had first obtained oxygen. Warltire drew Priestley's attention to the fact that after the explosion the sides of the glass vessel were bedewed with moisture. Neither of the experimenters attached any importance to the circumstance at the time, Priestley being of opinion that the moisture was pre-existent in the gases, as no special pains were taken to dry them. Warltire, however, conceived the notion that the experiment would afford the means of determining whether heat was ponderable or not, and hence he was led to repeat it, firing the mixture in a copper vessel for

greater safety. The results of these observations are contained in Priestley's "Experiments and Observations on Air," vol. v. 1781, App. p. 395.

At this period Cavendish was engaged on a series of experiments "made, as he says, principally with a view to find out the cause of the diminution which common air is well known to suffer by all the various ways in which it is phlogisticated, and to discover what becomes of the air thus lost or condensed" (Cavendish, *Phil. Trans.* 1784, p. 119). On the publication of Priestley's work he repeated Warltire's experiment, for, he says, as it "seemed likely to throw great light on the subject I had in view, I thought it well worth examining more closely." The series of experiments which Cavendish was thus induced to make, and which he made with all his wonted skill in quantitative work, led him some time in the summer of 1781 to the discovery that a mixture of two volumes of the inflammable air from metals (the gas we now call hydrogen) with one volume of the dephlogisticated air of Priestley combine together under the influence of the electric spark, or by burning, to form the same weight of water. If Cavendish had published the results of these observations at or near the time he obtained them, there would have been no Water Controversy. But in the course of the trials he found that the condensed water was sometimes acid, and the search for the cause of the acidity (which incidentally led to the discovery of the composition of nitric acid) occasioned the delay. The main result that a mixture of two volumes of inflammable air and one volume of dephlogisticated air could be converted into the same weight of water was, however, communicated to Priestley, as he relates in a paper in the *Phil. Trans.* for 1783. Priestley was at this time interested in an investigation on the seeming convertibility of water into air, and he was led to repeat Cavendish's experiments, some time in March 1783, on what was apparently the converse problem. Priestley, however, made a fatal blunder in the repetition. With the praiseworthy idea of obviating the possibility of any moisture in the gases, he prepared the dephlogisticated air from nitre, and the inflammable air by heating what he calls "perfectly made charcoal" in an earthenware retort. At this time, it must be remembered, there was no sharp distinction between the various kinds of inflammable air: hydrogen, sulphuretted hydrogen, marsh gas and olefiant gas, coal gas, the vapours of ether and turpentine, and the gas from heated charcoal, consisting of a mixture of carbonic oxide, marsh gas, and carbonic acid, were indifferently termed "inflammable air." Priestley attempted to verify Cavendish's conclusion on the identity of the weight of the gases used with that of the water formed; but his method in this respect, as in his choice of the inflammable air, was wholly defective, and could not possibly have given him accurate results. It consisted in wiping out the water from the explosion vessel by means of a weighed piece of blotting-paper and determining the increase of weight of the paper. He says, however, "I always found, as near as I could judge, the weight of the decomposed air in the moisture acquired by the paper. . . . I wished, however, to have had a nicer balance for this purpose; the result was such as to afford a strong presumption that the air was reconverted into water, and therefore that the origin of it had been water." These results, together with those on the conversion of water into air, were communicated towards the end of March, 1783, by Priestley to Watt, who began to theorise upon them, and then to put his thoughts together in the form of a letter to Priestley, dated April 26, 1783, and which he requested might be read to the Royal Society on the occasion of the presentation of Priestley's memoir. In this letter Watt says:—"Let us now consider what obviously happens in the case of the deflagration of the inflammable and dephlogisticated air. These two kinds of air unite with violence, they become red-hot, and upon cooling totally disappear. When the vessel is cooled, a quantity of water is found in it equal to the weight of the air employed. This water is

then the only remaining product of the process, and water, light, and heat are all the products. Are we not then authorised to conclude that water is composed of dephlogisticated air and phlogiston deprived of part of their latent or elementary heat; that dephlogisticated or pure air is composed of water deprived of its phlogiston and united to elementary heat and light, &c.?"

This letter, although shown to several Fellows of the Society, was not publicly read at the time intended. Priestley, before its receipt, had detected the fallacy of his experiments on the seeming conversion of water into air, and as much of the letter was concerned with this matter Watt requested that it should be withdrawn. Watt, however, as he tells Black* in a letter dated June 23, 1783, had not given up his theory as to the nature of water, and on November 26, 1783, he re-stated his views more fully in a letter to De Luc. In the meantime Cavendish, having completed one section of his investigation, sent in a memoir to the Royal Society, which was read on January 15, 1784, in which he gives an account of his experiments and announces his conclusion "that dephlogisticated air is in reality nothing but dephlogisticated water, or water deprived of its phlogiston; or, in other words, that water consists of dephlogisticated air united to phlogiston; and that inflammable air is either pure phlogiston, as Dr. Priestley and Mr. Kirwan suppose, or else water united to phlogiston." Watt thereupon requested that his letter to De Luc should be published, and it was accordingly read to the Royal Society on April 29, 1784. Which of the two—Cavendish or Watt—is, under these circumstances, to be considered as "the true and first discoverer" of the compound nature of water is the question which has been hitherto the main subject of the water controversy.

Let us now consider the matter as it affects Lavoisier. In 1783 Lavoisier had publicly declared against the doctrine of phlogiston, or rather, as M. Dumas puts it, "against the crowd of entities of that name which had no quality in common except that of being intangible by every known method." (*Leçons sur la Philosophie Chimique*, p. 161). How completely Lavoisier had dissociated himself from the theory may be gleaned from his memoir of that year. "Chemists," he says, "have made a vague principle of phlogiston which is not strictly defined, and which in consequence accommodates itself to every explanation into which it is pressed. Sometimes this principle is heavy and sometimes it is not; sometimes it is free fire and sometimes it is fire combined with the earthy element; sometimes it passes through the pores of vessels and sometimes they are impenetrable to it: it explains at once causticity and non-causticity, transparency and opacity, colours and the absence of colours. It is a veritable Proteus which changes its form every moment."

But Lavoisier had merely renounced one fetish for another. At the time that he penned these lines he was as much under the thralldom of *le principe oxygène* as the most devoted follower of Stahl was in the bondage of phlogiston. The idea that the calcination of metals was but a slow combustion had been fully recognised. M. Berthelot tells us that as far back as the March of 1774 Lavoisier had written in his laboratory journal:—"I am persuaded that the inflammation of inflammable air is nothing but a fixation of a portion of the atmospheric air, a decomposition of air. . . . In that case in every inflammation of air there ought to be an increase of weight," and he tried to ascertain this by burning hydrogen at the mouth of a vessel from which it was being disengaged. In the following year he asks, what remains when inflammable air is burnt completely? According to the theory by which he is now swayed it should be an acid, and he made many attempts to capture this acid. In 1777 he and Berquet burnt six pints of the inflammable air from metals in a bottle containing lime-water, in the expecta-

tion that fixed air would be the result. And, in 1781, he repeated the experiment with Gengembre, with the modification that the oxygen was caused to burn in an atmosphere of hydrogen, but not a trace of any acid product could be detected. Of course there must have been considerable quantities of water formed in these experiments, but Lavoisier was pre-occupied with the conviction that oxidation meant acidification, and its presence was unnoticed, or, if noticed, was unheeded. Macquer, in 1776, had drawn attention to the formation of water during the combustion of hydrogen in air, but Lavoisier had stated that he was ignorant of that observation. What was it, then, that put him on the right track? We venture to think that M. Berthelot has himself supplied the answer. He says (p. 114) "rumours of Cavendish's trials had spread throughout the scientific world during the spring of 1783. . . . Lavoisier, always on the alert as to the nature of the products of the combustion of hydrogen, was now in such position that the slightest hint would enable him to comprehend its true nature. He hastened to repeat his trials, as he had the right to do, never having ceased to occupy himself with a question which lay at the very heart of his doctrine."

"On the 24th of June, 1783," continues M. Berthelot, "he repeated the combustion of hydrogen in oxygen, and he obtained a notable quantity of water without any other product, and he concluded from the conditions under which he had worked that the weight of the water formed could not be other than equal to that of the two gases which had formed it. The experiment was made in the presence of several men of science, among whom was Blagden, a member of the Royal Society of London, who on this occasion recalled the observations of Cavendish (*qui rappela à cette occasion les observations de Cavendish*)."

On the following day Lavoisier published his results. The following is the official minute of the communication taken from the register of the sittings of the Académie des Sciences:—

Meeting of Wednesday, June 25, 1783.

MM. Lavoisier and De Laplace announced that they had lately repeated the combustion of Combustible Air with Dephlogisticated Air; they worked with about 60 pints of the airs, and the combustion was made in a closed vessel: the result was very pure water.

The cautious scribe who penned that minute did not commit himself too far. M. Berthelot, however, regards it as the first certain date of publication, established by authentic documents, in the history of the discovery of the composition of water, "a discovery," he adds, "which, on account of its importance, has excited the keenest discussion."

You will search in vain through the laboratory journals as given by M. Berthelot, for any indications either of experiments or reflections which would enable you to trace the course of thought by which Lavoisier was guided to the truth. There is absolutely nothing on the subject until in the eighth volume (25 mars, 1783, au février 1784), and on p. 63 we come to the experiment of June 24, and we read:—"In presence of Messieurs Blagden, of [name illegible], de Laplace, Vandermonde, de Fourcroy, Meusnier, and Legendre, we have combined in a bell-jar dephlogisticated air and inflammable air drawn from iron by means of sulphuric acid, &c. . . . The amount of water may be estimated at 3 drachms: the amount which should have been obtained was 1 ounce 1 drachm and 12 grains. Thus we must suppose that there was a loss of two-thirds of the amount of the air or that there has been a loss of weight.

And this is the experiment which, according to M. Berthelot, enabled Lavoisier to conclude that "the weight of the water formed could not be other than equal to that of the two gases which had formed it!" It is on this single experiment, hurriedly and imperfectly done, that Lavoisier's claim to the discovery of the compound

* Watt, *Correspondence*, p. 31.

nature of water is based! M. Berthelot objects to the assumption that it was hurriedly done. He says, on p. 114:—"Lavoisier caused a new apparatus to be made, with a couple of tubes and two reservoirs for the gases, an arrangement which would require a certain amount of time to put together; this circumstance proves that it could not have been an improvised trial." To what extent it was improvised will be seen immediately.

Now, although the laboratory journals do not in this case "inform us of Lavoisier's methods, and of the direction of his mind . . . the successive steps in the evolution of his private thought," we have other means of ascertaining how he arrived at his knowledge. The method was simplicity itself: he was told of the fact, and his informant was none other than Cavendish's assistant, Blagden.

Cavendish's memoir was published in 1784. Before it was struck off its author caused the following addition to be made:—"During the last summer also a friend of mine gave some account of them [the experiments] to M. Lavoisier, as well as of the conclusion drawn from them, that dephlogisticated air is only water deprived of phlogiston; but at that time so far was M. Lavoisier from thinking any such opinion warranted that, till he was prevailed upon to repeat the experiment himself, he found some difficulty in believing that nearly the whole of the two airs could be converted into water." This addition, as I have had the opportunity of verifying by an inspection of the original MSS. in the archives of the Royal Society, was made in the handwriting of Cavendish's assistant and amanuensis, Blagden.

When Lavoisier's memoir appeared it was found to contain the following reference to this circumstance:—"It was on the 24th of June that M. de Laplace and I made this experiment in presence of MM. le Roi, Vandermonde, and several other Academicians, and of Mr. Blagden, the present Secretary of the Royal Society of London. The latter informed us (*ce dernier nous apprit*) that Mr. Cavendish had already tried, in London, to burn inflammable air in closed vessels, and that he had obtained a very sensible quantity of water."

This reference was so partial, and its meaning so ambiguous, that Blagden addressed the following letter to Crell to be published in his "Chemische Annalen" (Crell's "Annalen," 1786, vol. i., p. 58).

It is so direct and conclusive that I offer no apology for giving it almost entire:—

"I can certainly give you the best account of the little dispute about the first discoverer of the artificial generation of water, as I was the principal instrument through which the first news of the discovery that had been already made was communicated to Mr. Lavoisier. The following is a short statement of the history:—

"In the spring of 1783 Mr. Cavendish communicated to me, and other members of the Royal Society, his particular friends, the result of some experiments with which he had for a long time been occupied. He showed us that out of them he must draw the conclusion that dephlogisticated air was nothing else than water deprived of its phlogiston; and, *vice versa*, that water was dephlogisticated air united with phlogiston. About the same time the news was brought to London that Mr. Watt, of Birmingham, had been induced by some observations to form a similar opinion. Soon after this I went to Paris, and in the company of Mr. Lavoisier and of some other members of the Royal Academy of Sciences I gave some account of these new experiments and of the opinions founded upon them. They replied that they had already heard something of these experiments, and particularly that Dr. Priestley had repeated them. They did not doubt that in such manner a considerable quantity of water might be obtained, but they felt convinced that it did not come near

to the weight of the two species of air employed, on which account it was not to be regarded as water formed or produced out of the two kinds of air, but was already contained in and united with the airs, and deposited in their combustion. This opinion was held by Mr. Lavoisier, as well as by the rest of the gentlemen who conferred on the subject; but, as the experiment itself appeared to them very remarkable in all points of view, they unanimously requested Mr. Lavoisier, who possessed all the necessary preparations, to repeat the experiment on a somewhat larger scale as early as possible. This desire he complied with on the 24th June, 1783 (as he relates in the latest volume of the Paris memoirs). From Mr. Lavoisier's own account of his experiment it sufficiently appears that at that period he had not yet formed the opinion that water was composed of dephlogisticated and inflammable airs, for he expected that a sort of acid would be produced by their union. In general, Mr. Lavoisier cannot be convicted of having advanced anything contrary to truth: but it can still less be denied that he concealed a part of the truth; for he should have acknowledged that I had, some days before, apprised him of Mr. Cavendish's experiments, instead of which the expression '*il nous apprit*' gives rise to the idea that I had not informed him earlier than that very day. In like manner Mr. Lavoisier has passed over a very remarkable circumstance, namely, that the experiment was made in consequence of what I had informed him of. He should likewise have stated in his publication not only that Mr. Cavendish had obtained '*une quantité d'eau très sensible*,' but that the water was equal to the weight of the two airs added together. Moreover, he should have added that I had made him acquainted with Messrs. Cavendish and Watt's conclusions, namely, that water, and not an acid, or any other substance, arose from the combustion of the inflammable and dephlogisticated airs. But those conclusions opened the way to Mr. Lavoisier's present theory, which perfectly agrees with that of Mr. Cavendish, only that Mr. Lavoisier accommodates it to his old theory, which banishes phlogiston. . . . The course of all this history will clearly convince you that Mr. Lavoisier (instead of being led to the discovery by following up the experiments which he and Mr. Bucquet had commenced in 1777) was induced to institute again such experiments, solely by the account he received from me, and of our English experiments; and that he really discovered nothing but what had before been pointed out to him to have been previously made out and demonstrated in England."

To this letter, reflecting so gravely on his honour and integrity, Lavoisier made no reply. Nor did Laplace, Le Roi, Vandermonde, or any one of the Academicians concerned vouchsafe any explanation. *De non apparentibus et de non existentibus eadem ratio*. No explanation appeared because none was possible. M. Berthelot ignores this letter, which is the more remarkable, since reference is made to it in more than one of the publications which he tells us he has consulted in the preparation of his account of the Water Controversy. If he knew of it he must regard it either as unworthy of an answer or as unanswerable.

It would be heaping Ossa on Pelion to adduce further evidence from letters of the time of what Lavoisier's contemporaries thought of his claims. *De mortuis nil nisi bonum*. I would much more willingly have dwelt upon the virtues of Lavoisier, and have let his faults lie gently on him; but I have felt it incumbent on me on this occasion to make some public answer to M. Berthelot's book, and in no place could that answer be more fittingly given than in this town, which saw the dawn of that work out of which these grand discoveries arose. It may be that much of what I have had to say is as a twice-told tale to many of you. I trust I need make no apology on that account. The honour of our ancestors is in our keeping, and we should be unworthy of our heritage and

* Mr. Muirhead's translation. Vide Watt, *Correspondence*, "Composition of Water," p. 71.

false to our trust if we were slow to resent or slack to repel any attempt to rob them of that glory which is their just right and our proud boast.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

In ascertaining the composition of a mixture of oils, I was guided, in my earlier experiments, by the condition of the products resulting from the treatment with sulphur chloride, and whilst it is quite possible to obtain a fair idea of what oils are present in a mixture, the products themselves give no definite information of the probable quantities; the Hubl reagent was worked on to supply this. The iodine absorption of the original oil or mixture is taken and also that of the soluble portion of the magma by sulphur chloride, the same quantities being used in each case. The iodine absorption is calculated, first, for the total weight equal to that of the original oil, and, secondly, for the corresponding weight obtained from a definite quantity of the original oil; this latter I shall refer to as the *corrected* iodine absorption of the soluble extract from the magma.

I prepare and use the Hubl reagent in the following way. 50 grms. pure re-sublimed iodine is dissolved in alcohol, sp. gr. 795 at 60° F., and made up to 500 c.c. 60 grms. mercuric chloride, in powder, dissolved in another portion of the same spirit, is filtered, and the spirit washings of the filter added to make up 500 c.c.; these solutions are kept separately in a cool, dark cupboard. When required equal parts of these solutions are mixed together just before being used, sufficient for the samples, &c., to be tested. The advantage of this is evident when only 30 or 40 c.c. Hubl is wanted, and, perhaps, in a hurry. The Hubl is standardised in the ordinary way with sodium thiosulphate, which is previously adjusted with pure and dry re-sublimed iodine.

The oil, &c., after digesting for the required time with the reagent and chloroform, is emptied into a stout glass and the flask rinsed out with 10 c.c. of a 10 per cent solution of KI and 40 c.c. water. It is again rinsed out with 100 c.c. water in two separate portions. During titration the whole is kept well stirred with an ebonite rod, so as to avoid scratching the glass. If mercuric iodide is precipitated on dilution, it is best to add KI in crystals rather than solution.

The sulphur chloride is prepared by distilling the commercial yellow chloride and collecting the portion coming over about 284° F.; the portion coming over under 284° may be digested with an excess of S, and distilling again when required. If the dark chloride only is available it should be digested with S for some time in a warm place before distilling. The prepared chloride may be kept for some time mixed with an equal volume of CS₂ in a stoppered bottle, the neck of which should be kept clean, so as to prevent the stopper getting fixed. The quantity required should be taken out with a fine pipette.

The bulk of chloride may be kept in a bottle well closed with a piece of paraffined merino or cotton, or an ordinary cork well soaked in paraffin may be used; however preserved it should be occasionally looked to and kept in a cool place.

The details of the process for using the chloride have already appeared in this journal.

If two oils be mixed together and we know the iodine absorption of each oil and of the mixture, a simple calculation will enable us to tell how much of each oil is present in the mixture.

A mixture of olive oil and sesame oil is found to have an iodine absorption = 96.4 per cent. Olive oil = 84.5 per cent, and sesame oil = 106 per cent. If we divide the iodine absorption of the mixture (96.4) into two parts, pro-

portional to the iodide absorption of olive oil (84.5) and sesame oil (106), we obtain the proportional quantities of iodine absorbed by each oil contained in the mixture:—

$$\frac{96.4}{84.5 + 106} \times 84.5 = 42.8 \text{ absorption due to olive oil}$$

$$,, \times 106 = 53.6 \text{ ,, ,, sesame oil}$$

In the same way, if we have obtained a fair clue of what a mixture contains, even if 3 or 4 oils are mixed together we can obtain an approximation for our first result; unfortunately the oils separately might be so altered in their original iodine absorption that our first approximation might yield a mixture quite unlike what we are trying to imitate, although the iodine absorption is exactly that of the sample.

A mixture of olive oil, lard oil, and linseed oil has an iodine absorption identical with olive oil = 84.5, lard oil = 52.5, and linseed oil = 170. The iodine absorption of such a mixture admits of a double rendering—we may either compound a mixture of linseed oil and lard oil which shall have an iodine absorption = olive oil, and which, of course, may be mixed in all proportions with olive oil without affecting the iodine absorption, or we may calculate for a mixture of the three oils

First Case.

$$\frac{84.5}{52.5 + 170} \times 52.5 = 19.95 = \text{iodine absorption due to lard oil}$$

$$,, \times 170 = 64.6 = \text{,, ,, linseed ,,}$$

Second Case.

$$\frac{84.5}{84.5 + 52.5 + 170} \times 84.5 = 23.24 \text{ iodine ,, olive ,,}$$

$$,, \times 52.5 = 14.44 \text{ ,, ,, lard ,,}$$

$$,, \times 170 = 46.75 \text{ ,, ,, linseed ,,}$$

In both cases the proportional absorptions for lard oil and linseed oil are the same as demanded by the original iodine absorption; for if we remove the olive oil, the remaining lard oil and linseed oil should have the same iodine absorption as olive oil.

The mixture is then made up as indicated by the second case, and examined side by side with the original mixture. Linseed oil and olive oil both yield insoluble products with sulphur chloride; the lard oil would be removed by CS₂, with more or less of the non-solidified products from the other oils, and which is subsequently examined by Hubl's reagent as given in this communication.

ON THE EFFECT OF TEMPERATURE UPON THE DETERMINATION OF AMMONIA BY NESSLERISATION.

By ALLEN HAZEN and HARRY W. CLARK.

IN making a number of distillations of standard ammonium chloride solution to determine the loss due to incomplete condensation, as stated by Dr. Smart,* results were obtained similar to those given by him, namely, that only from 85 to 95 per cent of the ammonia taken was found in the distillate. It was observed, however, that no more ammonia was obtained when the end of the condenser dipped below the surface of cold water, and also that by repeatedly re-distilling a distillate from standard ammonium chloride solution, no more was lost than by a single distillation. The loss could not therefore be due to incomplete condensation.

The cause of this apparent loss was found to be the low temperature of the distillates. The city water, at a

* "Report of the National Board of Health," 1882; also the *American Chemical Journal*, xi., 367.

temperature of 5°, running about the block tin condensers, cooled the distillate to nearly the same temperature, and the time that the tubes stood before Nesslerising was insufficient to warm them to the temperature of the room. It was found that the colour obtained by Nesslerising an ammonia solution depends upon its temperature. The warmer the solution the deeper will be the colour produced, so that a standard containing 4 c.c. of ammonia solution Nesslerised at 30° will give a colour equal to that obtained from 5 c.c. Nesslerised at 15°, or 6 c.c. Nesslerised at 0°. A change in temperature after Nesslerising will not change the colour very much.

To obtain accurate results it is necessary to bring standards and distillates to the same temperature before Nesslerising. This is easily accomplished by allowing them to stand in a room with even temperature for a sufficient time. It was found that the difference between the temperatures of two 50 c.c. Nessler tubes of water, standing side by side, was reduced to one-half every thirteen minutes. With racks of three dozen tubes each the adjustment was much slower, forty-five minutes being required to reduce a difference of 10° 5°. When the possible difference of temperature between different tubes at the start is 10° or more, three or four hours will be required to bring them to a sufficiently even temperature. We find it most convenient to let them stand over night. Standards and distillates are made ready for Nesslerisation during the day, and all stand on the same table over night. In the morning they are Nesslerised and compared. There is not the slightest loss by evaporation of ammonia in this way, even upon standing some days, and in a laboratory where ammonia fumes are excluded there is no danger of absorption of ammonia from the air.

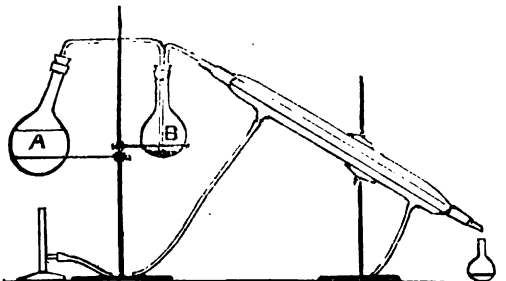
Our earlier conclusion, that there is no loss of ammonia by incomplete condensation, has been confirmed by numerous determinations made in this way, with most satisfactory results. The condenser tubes used are of block tin, 20 inches long and $\frac{3}{8}$ inch internal diameter.—*American Chemical Journal*, xii., No. 6.

APPARATUS FOR THE DETERMINATION OF AMMONIAS IN SAND AND SEWAGE.

By ALLEN HAZEN.

In examining sand from filters it has been thought desirable to determine free and albumenoid ammonia, as this shows the amount of organic matter stored in the same terms as it is given for the filtered water or sewage.

To accomplish this the apparatus shown by the figure has been used during the last two years. A litre flask, A,



filled with ammonia-free water, serves simply to supply steam. A small glass tube carries the steam to the bottom of the small flask, B, which contains the sand. The steam passing through the sand very rapidly removes all free ammonia. Alkaline permanganate solution is then put in B and the distillation continued. The albumenoid ammonia is given off much more rapidly than in the ordinary water distillation, owing to the concentration of the permanganate which is put upon the sand full

strength, while in water-analysis it is diluted to eight of ten times its volume by the water. One portion of 50 c.c. invariably contains all the free ammonia. The first portion of albumenoid ammonia, when boiling rapidly, usually contains at least eight or nine tenths of the whole, and the second portion has almost all of the rest, so that only two tubes need be collected. Bumping is impossible. The condensation of steam in the small flask is not excessive, but if necessary it may be heated with a low flame.

I have found this apparatus to be well adapted to the examination of sewage and anything which contains enough ammonia. The great bulk of a pure water which it would be necessary to use prevents its application to ordinary water-analysis.

The amount of free ammonia thus obtained is the same as that found by the usual process of dilution with pure water and direct distillation. The albumenoid ammonia is commonly a little greater, owing to the concentration of the permanganate, but the results are sharper and different determinations agree with each other more closely. There is also a very considerable saving of time when a number of determinations are to be made.

I prefer to use rubber stoppers and connections. It requires considerable boiling to get new rubber entirely free from ammonia, but once free there is no more trouble, and a stopper will last for a very long time.—*American Chemical Journal*, xii., No. 6.

OBITUARY.

PROFESSOR THOMAS CARNELLEY.

ON the 27th ult. the chemical world sustained a severe and unexpected blow by the sudden death of Prof. Thomas Carnelley. He was only in his thirty-eighth year, and all who knew him naturally hoped that he might continue doing excellent work for at least a quarter of a century. The deceased was educated at University College, London. His first appointment was that of Demonstrator of Chemistry at the Owens College, Manchester. He then occupied successively the Chemical Chair at Firth College, Sheffield, and at the Universities of Dundee and Aberdeen.

His work included especially the further development of the periodic system of Newlands and Mendeleeff, to which he made most important contributions. Up to the time of his death he was engaged upon a great work on the chemical and physical constants, in which he was tracing out relations and uniformities not previously detected. Whether this, his *magnum opus*, is sufficiently advanced to be capable of publication we are unable to say. Prof. Carnelley likewise carried on some investigations on questions of sanitary chemistry. Thus he published an investigation of the sanitary condition of Board Schools, &c., in Scotland and England, with especial reference to the prevalence of microbia in their atmospheres. The last article from his pen which appeared in the *CHEMICAL NEWS* was an account of researches undertaken in concert with Mr. W. Frew on "The Antiseptic Powers of Isomeric Organic Compounds." Thomas Carnelley was a man whom the scientific world could ill spare.

ERRATUM.—P. 97, col. 1, line 21 from bottom, for " $\text{Ni}(\text{CO})_4$ " read " $\text{Ni}(\text{CO})_5$."

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LEEDS, 1890.

INAUGURAL ADDRESS OF THE PRESIDENT,

SIR FREDERICK AUGUSTUS ABEL,
C.B., D.C.L. (Oxon.), D.Sc. (Cant.), F.R.S., P.P.C.S.
Hon. M.Inst.C.E.

Concluded from p. 118).

THE Crimean War taught Nations many lessons of gravest import, to some of which Sir Richard Owen took occasion to call attention most impressively in the address delivered here, before the miseries of that war had become past history. The development of sanitary science, to which he especially referred, and which sprang from the bitter experience of that sad epoch, has had its parallel in the development of the science of artillery; but it would indeed be difficult to establish any parallelism between the benefits which even the soldier and sailor have reaped from the great strides made by both these sciences. The acquisition of knowledge of the causes of the then hopelessness of gallant struggles which medical skill and self-sacrificing devotion made against the sufferings of the victims of battles and of fell diseases, as deadly as the cruellest implements of war; the application of that knowledge to the provision of the blessings of antiseptic treatment of wounds and to the intelligent utilisation of disinfectants and of other valuable preventive measures, to the supply of wholesome water, of wholesome food in campaigning, of sensible clothing, and of wholesome air in hospitals, barracks, and ships—these are some few of the benefits which the soldier and the sailor have derived from the development of sanitary science, which was so powerfully stimulated by the terrible lessons learned during the long-drawn-out siege of Sebastopol; and it is indeed pleasant to reflect that there has been, for years past, most wholesome competition between Nations in the enlargement of those benefits, and their dissemination among the men whose vocation it is to slay and be slain. The periodical International Congresses on Hygiene and Demography, of which we shall cordially welcome next year's assemblage in London, and whose members will deplore the absence from among them of the veteran Nestor in the science and practice of hygiene, Sir Edwin Chadwick, have afforded conclusive demonstration of the heartiness with which Nations are now co-operating with a view to utilise the invaluable results attained by the successful labourers in sanitary science.

What, on the other hand, shall we say of the benefits which sailors and soldiers, in the pursuit of their calling, derive from the ceaseless costly competition amongst Nations for supremacy in the possession of formidable artillery, violent explosives, quick-firing arms of deadly accuracy, and fearful engines which, unseen, can work wholesale destruction in a fleet? And what can we say of the benefits acquired by individual countries in return for their continuous, and sometimes ruinous, expenditure in endeavouring to maintain themselves upon an equality with their neighbours in man-killing power? The conditions under which engagements by sea or land will in the future be fought have certainly become greatly modified from those of thirty-five years ago, and the duration of warfare, even between Nations in conflict who are on a

fair equality of resources, must become reduced; but, as regards the results of a trial of strength between contending forces, similarly equipped, as they now will be, with the latest of modern appliances only varying in detail, these must, after all, depend, as of old, partly upon accident, favoured, perhaps, by a temporary superiority in equipment, partly upon the skill and military genius of individuals, and very much upon the characteristics of the men who fight the battles.

What really can be said in favour of the advances made in the appliances of war—and this is, perhaps, the view which in such a town as Leeds we should keep before our eyes to the exclusion of the dark side of the picture—is, that by continuous competition in the development of their magnitude, diversity, and perfection, the resources of the manufacturer, the chemist, the engineer, the electrician, are taxed to the uttermost, with the very important, although incidental, results, that industries are created or expanded and perfected, trades maintained and developed, and new achievements accomplished in applied science, which in time beneficially affect the advance of peaceful arts and manufactures. In these ways the expenditure of a large proportion of a country's resources upon material which is destroyed in creating destruction does substantially benefit communities, and tends to the accomplishment of such material progress by a country as goes far to compensate its people for the sacrifices which they are called upon to incur for the maintenance of their dignity among Nations.

From this point of view, at any rate, it may interest members of the British Association for the Advancement of Science, and for the promotion of its applications to the welfare and happiness of mankind, to hear something of recent advances in one of the several branches of science in its applications to naval and military requirements with which, during a long and arduous official career, now approaching its close, I have become in some measure identified.

Since the meeting of the Association in this town in 1858, the progress which has been made in the regulation of the explosive force of gunpowder, so as to adapt it to the safe development of very high energy in guns presenting great differences in regard to size and to the work which they have to perform, has been most important. The different forms of gunpowder which were applied to war purposes in this and other countries, until within the last few years, presented comparatively few differences in composition and methods of manufacture from each other and from the gunpowder of our ancestors. The replacement of smoothbore guns by rifled artillery, which followed the Crimean War, and the great increase in the size and power of guns, necessitated by the application of armour to ships and forts, soon called, however, for the pursuit of investigations having for their object the attainment of means for variously modifying the action of fired gunpowder, so as to render it suitable for artillery of different calibres whose power could not be effectively, or, in some instances, safely, developed by the use of the only kind of gunpowder then employed in English artillery of all calibres.

The means resorted to in the earlier of these investigations, and adhered to for many years, for controlling the violence of explosion of gunpowder, consisted exclusively in modifying the size and form of the individual masses composing a charge, and of their density and hardness, with the object of varying the rate of burning of those masses in a gun; it being considered that, as the proportions of ingredients generally employed very nearly correspond to those required for the development of the greatest chemical energy by the thoroughly-incorporated materials, the attainment of the desired results should be, if possible, effected rather by modifications of the physical and mechanical characters of gunpowder, than by variations of the proportions and chemical characters of its ingredients.

The varieties of powder from time to time introduced

into artillery-service, as the outcome of investigations in this direction, were of two distinct types: the first of these consisted of further developments of the old granulated or corned powder, being produced by breaking up more or less highly-pressed slabs of the material into grains, pebbles, or boulders of approximately uniform size and shape. Gunpowders of this class, ranging in size from about 1000 pieces to the ounce to about 6 pieces to the pound, have performed efficient service, and certain of them are still employed. The character of the other type is based upon the theoretical view that uniformity in the action of a particular gunpowder, when employed under like conditions, demands not merely identity in regard to composition, but also identity in form, size, density, and structure of the individual masses of which a charge consists. To approach the practical realisation of this view, equal quantities of one and the same mixture of ingredients, presented in the form of powder of uniform fineness and dryness, must be submitted to a particular pressure, for a fixed period, in moulds of uniform size, the surrounding conditions and subsequent manufacturing processes being as nearly as possible alike. Practical experience has shown that uniformity in the ballistic properties of black powder can be even more readily secured by the thorough blending or mixing together of different products of manufacture, presenting some variations in regard to size, density, hardness, or other features, than by aiming at an approach to identity in the characters of the individual grains or masses.

When our attention was first actively directed to the modification of the ballistic properties of powder, the subject had already been to some extent dealt with in the United States by Rodman and Doremus, and the latter had proposed the employment, in heavy guns, of charges consisting of large pellets of prismatic form. While this prismatic powder, which was first used in Russia, was being perfected, and extensively applied there as well as in Germany and England, the production of powder-masses more suitable, by the comparatively gradual nature of their explosion, for the very large charges required for the heavy artillery of the present day, was actively pursued in Italy, and by our own Government Committee on Explosives, the outcome of very exhaustive practical investigations being the very efficient Fossano powder, or *poudre progressif* of the Italians, and the boulder and large cylindrical powders produced at Waltham Abbey.

Researches carried out by Captain Noble and myself some years ago, with a series of gunpowders, presenting considerable differences in composition, indicated that decided advantages might be secured, for heavy guns especially, by the employment of such a powder as would furnish a comparatively very large volume of gas, its explosion being at the same time attended by the development of much less heat than in the case of ordinary black powder. In the course of these researches much light was thrown upon the causes of the wearing or erosive action of powder-explosions upon the inner surface of the gun, an action which, especially in the larger calibres of artillery, produces so serious a deterioration of the arm that the velocity of projection and accuracy of shooting suffer considerably, the wear being especially great where the products of explosion, while under the maximum pressure, can escape between the projectile and the bore. The great velocity with which the very highly heated gaseous and liquid (fused solid) products of explosion sweep over the heated surface of the metal, gives rise to a displacement of the particles composing the surface of the bore, which increases in extent as the latter becomes roughened, and thus opposes greater resistance; at the same time, the high temperature to which the surface is raised reduces the rigidity of the metal, and its consequent power of resisting the force of the gaseous torrent; and, lastly, some amount of chemical action upon the metal, by certain of the highly-heated non-gaseous products of explosion, contributes towards an increase in the erosive

effects. Experiments made upon a large scale by Captain Noble with powders of different composition, and with other explosives, have afforded decisive evidence that the explosive agent which furnishes the largest proportion of gaseous products, and the explosion of which is attended by the development of the smallest amount of heat, exerts least erosive action.

Some eminent German gunpowder manufacturers, who were at this time actively engaged upon the production of a suitable powder for heavy guns, directed their attention, not merely to an alteration of the proportions of the ingredients, but also to a modification in the character of charcoal employed; the eventual result was the production of a new prismatic powder, composed of saltpetre in somewhat higher proportion than in normal black powder, and of a very slightly-burned charcoal of reddish brown colour, quite similar to the *charbon roux* which Violette produced about forty years ago for use in sporting-powder, by the action of super-heated steam upon wood or other vegetable matter. This brown prismatic powder (or "cocoa powder") differs from black powder not merely in colour: it burns very slowly in the open air, and in guns its action is comparatively gradual and long-sustained. The products of its explosion are simple; as the powder contains saltpetre in large proportion relatively to the sulphur and charcoal, these become fully oxidised, and a relatively very large amount of water-vapour is produced, partly because of the comparatively high proportion of water in the finished powder, and partly from the large amount of hydrogen in the slightly-charred wood or straw used. The smoke from a charge of brown powder differs but little in volume from that of black powder, but it disperses much more rapidly, owing to the speedy absorption of the finely-divided potassium salts, forming the smoke, by the large proportion of water-vapour through which they are distributed.

This kind of powder has been substituted, with considerable advantage, for black powder in guns of comparatively large calibre, but it soon became desirable to attain even more gradual action in the case of the very large charges required for guns of the heaviest calibres, such as the 110-ton gun, from which shot of about 1800 lbs. weight are propelled by a powder-charge of 960 lbs. Brown powder has, therefore, been modified in composition to suit these conditions; while, on the other hand, a powder intermediate in rapidity of action between black powder and the brown prism powder has been found more suitable than the former for use in guns of moderately large calibre.

The importance which machine-guns and comparatively large quick-firing guns have assumed in the armament of ships has made it very desirable to provide a powder for them which will produce comparatively little or no smoke, as their efficient employment becomes greatly limited when, after a very few rounds rapidly fired with black powder, the objects, against which it is desired to direct the fire, are more or less completely hidden by the interposed smoke. Hence much attention has of late been directed to the production of smokeless, or nearly smokeless, powders for naval use. At the same time, the views of many military authorities regarding the importance of dispensing with smoke in engagements on land, have also created a demand for smokeless powders suitable for field-artillery and for small arms.

The properties of ammonium nitrate, of which the products of decomposition by heat are, in addition to water-vapour, entirely gaseous, have rendered it a tempting material to those who have striven to produce a smokeless powder; but its deliquescent character has been a formidable obstacle to its application as a component of a useful explosive agent. By incorporating charcoal and saltpetre in particular proportions with ammonium nitrate, F. Gaus recently claimed to have produced an explosive material free from the hygroscopic character common to other ammonium nitrate mixtures, and furnishing only permanently gaseous and volatile, or

smokeless, products of explosion. These anticipations were not realised, but they led the talented German powder-maker, Mr. Heidemann, to produce an ammonium nitrate powder possessing remarkable ballistic properties, and producing comparatively little smoke, which speedily disperses. It yields a very much larger volume of gas and water-vapour than either black or brown powder, and is considerably slower in action than the latter; the charge required to produce equal ballistic results is less, while the chamber-pressure developed is lower, and the pressures along the chase of the gun are higher, than with brown powder. No greater tendency is exhibited by it to absorb moisture from an ordinarily dry, or even somewhat moist, atmosphere, but it rapidly absorbs water when the hygroscopic condition of the air approaches saturation, and this greatly restricts its use.

About five years ago reports began to reach us from France of the attainment of remarkable results with a smokeless powder employed with the repeating or magazine rifle then in course of adoption for military service, and of marvellous velocities obtained by the use of this powder, in specially constructed artillery of great length. As in the case of the explosive agent called *Mélinite*, the fabulously destructive effects of which were much vaunted at about the same time, the secret of the nature of this smokeless powder was well preserved by the French authorities; it is now known, however, that more than one smokeless explosive has succeeded the original, and that the material at present in use with the Lebel repeating rifle belongs to a class of nitro-cellulose or nitro-cotton preparations, of which several have been made the subject of patents in England, and of which varieties are also being used in Germany and other countries.

A comparison between the chemical changes attending the burning or explosion of gunpowder, and of the class of nitro-compounds represented by gun-cotton, at once explains the cause of the production of smoke by the former, and of the smokelessness of the latter. Whilst the products of explosion of the nitro-compounds consist exclusively of gases and of water-vapour, gunpowder, being composed of a large proportion of saltpetre, or other metallic nitrate, mixed with charred vegetable matter and variable quantities of sulphur, furnishes products of which over 50 per cent are not gaseous, even at high temperatures, and which are in part deposited as a fused solid—which constitutes the fouling in a fire-arm—and in part distributed in an extremely fine state of division through the gases and vapours developed by the explosion, thus giving to these the appearance of smoke as they escape into the air.

So far as smokelessness is concerned, no material can surpass *gun-cotton* (or other varieties of nitro-cellulose); but, even if the rate of combustion of the fibrous explosive in a firearm could be controlled with certainty and uniformity, its application as a safe propulsive agent is attended by so many difficulties that the non-success of the numerous early attempts to apply it to that purpose is not surprising. Those attempts, commencing soon after the discovery of *gun-cotton*, in 1846, and continued many years later in Austria, consisted entirely in varying the density and mechanical condition of employment of the *gun-cotton* fibre. No difficulty was experienced in thus exercising complete control over the rapidity of burning in the open air; but when the material was strongly confined, as in the bore of a gun, such methods of regulating its explosive force were quite unreliable, as some slight unforeseen variation in its compactness or in the amount and disposition of the air-spaces in the mass, would develop very violent action. Much more promising results were subsequently obtained by me by reducing the fibre to a pulp as in the ordinary process of making paper, and converting this into highly-compressed homogeneous masses of the desired form and size. Some favourable results were obtained at Woolwich in 1867-8 in field-guns, with cartridges built up of compressed *gun-cotton* variously formed and arranged, with the object of

regulating the rapidity of explosion of the charge. But although comparatively small charges often gave high velocities of projection without any indications of injury to the gun, the uniform fulfilment of the conditions essential to safety proved to be beyond absolute control, even in guns of small calibre; and military authorities not being in those days alive to the advantages which might accrue from the employment of an entirely smokeless explosive in artillery, experiments in this direction were not persevered in. At the same time, considerable success attended the production of *gun-cotton* cartridges for sporting purposes, the rapidity of its explosion being controlled by various methods; very promising results were also attained with the Martini-Henry rifle and a lightly-compressed pulped *gun-cotton* charge, of pellet-form, the uniform action of which was secured by simple means.

A nearly smokeless sporting powder had, in the meantime, been produced by Colonel Schultze, of the Prussian Artillery, from finely-divided wood, converted after purification into a mildly explosive form of nitro-cellulose, and impregnated with a small portion of an oxidising agent. Subsequently this powder was produced in a granular form, and rendered considerably more uniform in character, and less hygroscopic; it then closely resembled the well-known E.C. sporting powder, which consists of a nitro-cotton reduced to pulp, incorporated with the nitrates of potassium and barium, and converted into grains through the agency of a solvent and a binding material. Both these powders produce very little smoke compared with black powder, but do not compete with the latter in regard to accuracy of shooting when used in military arms.

In past years both camphor and liquid solvents have been applied to the hardening of the surfaces of granulated or compressed masses of *gun-cotton* and of this class of its preparations, with a view to render them non-porous. In some smokeless powders of French, German, Belgian, and English manufacture, acetic ether and acetone have been also used, not merely to harden the granules or tablets of the explosive, but to convert the nitrocellulose, in the first instance, into a more or less gelatinous condition, so that it can readily be incorporated with other components and rolled, or spread into sheets, or pressed into moulds, or squirted into wires, rods, or tubes, while still in a plastic state. When the solvent has afterwards been removed, the hardened, horn-like, or somewhat plastic product is cut up into tablets, or into strips or pieces of suitable dimensions, for conversion into charges or cartridges.

Another class of smokeless powder, similar in physical characteristics to these nitrocellulose powders, but containing nitroglycerin as an important component, has been originated by Mr. Alfred Nobel, the well-known inventor of dynamite, and bears resemblance in its physical characteristics to another of his inventions, called blasting-gelatin, one of the most interesting of known violent explosive agents. When one of the lower products of nitration of cellulose is impregnated with the liquid explosive, nitroglycerin, it gradually loses its fibrous nature, becoming gelatinised while assimilating the liquid; and the resulting product almost possesses the characters of a compound. This preparation, and certain modifications of it, have acquired high importance as blasting agents more powerful than dynamite, and possessed of the valuable property that their prolonged immersion in water does not separate from them any appreciable proportion of nitroglycerin. The nitroglycerin powder first produced by Mr. Nobel was almost perfectly smokeless and developed very high energy, accompanied by moderate pressures at the seat of the charge, but it possessed certain practical defects, which led to the development of several modifications of that explosive and various improvements in manufacture. The relative merits of this class of smokeless powder, and of various kinds of nitro-cellulose powder, are now under careful investigation in

this and other countries, and several more or less formidable difficulties have been met with in their application, in small-arms especially; these arise in part from the comparatively great heat they develop, which increases the erosive effects of the products of explosion, and in part from the more or less complete absence of solid products. The surfaces of the barrel and of the projectile being left clean, after the firing, are in a condition favourable to their close adhesion while the bullet is propelled along the bore, with the consequent establishment of very greatly increased friction. The latter difficulty has been surmounted by more than one expedient, but always at the cost of absolute smokelessness.

Our knowledge of the results obtained in France and Germany with the use of smokeless powders in the new rifles and in artillery is somewhat limited; our own experiments have demonstrated that satisfactory results are attainable with more than one variety of them, not only in the new repeating-arm of our infantry, but also with our machine-guns, with field-artillery, and with the quick-firing guns of larger calibre which constitute an important feature in the armament of our Navy. The importance of ensuring that the powder shall not be liable to undergo chemical change detrimental to its efficiency or safety, when stored in different localities where it may be subject to considerable variations of temperature (a condition especially essential in connection with our own Naval and Military service in all parts of the world), necessitates qualities not very easily secured in an explosive agent consisting mainly of the comparatively sensitive nitro-compounds to which the chemist is limited in the production of a smokeless powder. It is possible, therefore, that the extent of use of such a material in our ships, or in our tropical possessions, may have to be limited by the practicability of fulfilling certain special conditions essential to its storage without danger or possible deterioration. If, however, great advantages are likely to attend the employment of a smokeless explosive, at any rate for certain Services, it will be well worth while to adopt such special arrangements as may be required for securing these without incurring special dangers; this may prove to be especially necessary in our ships of war, where temperatures so high as to be prejudicial even to ordinary black powder, sometimes prevail in the magazines, consequent mainly upon the positions assigned to them in the ships, but which may be guarded against by measures not difficult of application.

The Press accounts of the wonderful performances of the first smokeless powder adopted by the French—which, it should be added, were in some respects confirmed by official reports of officers who had witnessed experiments at a considerable distance—engendered a belief that a very great revolution in the conduct of campaigns must result from the introduction of such powders. It was even reported very positively that noiselessness was one of the important attributes of a smokeless powder, and highly-coloured comparisons have, in consequence, been drawn in Service-periodicals, and even by some military authorities, between the battles of the past and those of the future: the terrific din caused by the firing of the many guns and the roar of infantry-fire, in heavy engagements, being supposed to be reduced to noise so slight that distant troops would fail to know in what direction their comrades were engaged, and that sentries and outposts would no longer be able to warn their comrades of the approaching foe by the discharge of their rifles. Military journals of renown, misled by such legendary accounts, chiefly emanating from France, referred to the absence of noise and smoke in battles as greatly enhancing the demands for skill and courage, and as surrounding a fight with mystery. The absence of recoil when a rifle was fired with smokeless powder was another of the marvels reported to attend the use of these new agents of warfare. It need scarcely be said that a closer acquaintance with them has dispelled the credit given to such of the accounts of their supposed qualities.

as were mythical, and a belief in which could only be ascribable to a phenomenal combination of credulity with ignorance of the most elementary scientific knowledge.

The extensive use which has been made in Germany of smokeless or nearly smokeless powder in one or two special military displays has, however, afforded interesting indications of the actual change which is likely to be wrought in the conditions under which engagements on land will be fought in the future, provided these new explosives thoroughly establish and maintain their position as safe and reliable propelling agents. Although the powder adopted in Germany is not actually smokeless, the almost transparent film of smoke produced by independent rifle-firing is not visible at a distance of about 300 yards; at shorter distances it presents the appearance of a puff of a cigar. The most rapid salvo-firing by a large number of men does not have the effect of obscuring them from distant observers. When machine guns and field artillery are fired with the almost absolutely smokeless powder which we are employing, their position is not readily revealed to distant observers by the momentary vivid flash of flame and slight cloud of dust produced.

There now appears little doubt that in future warfare belligerents on both sides will alike be users of these new powders; the screening or obscuring effect of smoke will therefore be practically absent during engagements between contending forces, and while, on the one hand, the very important protection of smoke, and its sometimes equally important assistance in manoeuvres, will thus be abolished, both combatants will, on the other hand, secure the advantages of accuracy of shooting and of the use of individual fire, through the medium of cover, with comparative immunity from detection. Such results as these cannot fail to affect, more or less radically, the principles and conditions under which battles have hitherto been fought. With respect to the Naval Service, it is especially for the quick firing guns, so important for defensive purposes, that a smokeless powder has been anxiously looked for; by the adoption of such a powder as has during the past year been elaborated for our artillery, should experience establish its reliability under all Service conditions and its power to fulfil all reasonable requirements in regard to stability, these guns will not only be used by our ships under conditions most favourable to their efficiency, but their power will also be very importantly increased.

The ready and safe attainment of very high velocities of projection through the agency of these new varieties of explosive agents, employed in guns of suitable construction, would appear at first sight to promise a very important advance in the power of artillery; the practical difficulties attending the utilisation of these results are, however, sufficiently formidable to place, at any rate at present, comparatively narrow limits upon our powers of availing ourselves of the advantages in ballistics which they may present. The strength of the gun-carriages and the character of the arrangements used for absorbing the force of recoil of the gun, need considerable modifications, not easy of application in some instances; greater strength and perfection of manufacture are imperative in the case of the hollow projectiles or shells to be used with charges of a propelling agent, by the firing of which in the gun they may be submitted to comparatively very severe concussions; the increased friction to which portions of the explosive contents of the shell are exposed by the more violent setting back of the mass may increase the possibility of their accidental ignition before the shell has been projected from the gun; the increase of concussion to which the fuse in the shell is exposed may give rise to a similar risk consequent upon an increased liability to a failure of the mechanical devices which are applied to prevent the igniting arrangement, designed to come into operation only upon the impact or graze of the projected shells, from being set into action prematurely by the shock of the discharge; lastly, the circumstance, that the rate of burning of the time-fuze which determines

the efficiency of a projected shrapnel shell is materially altered by an increase in the velocity of flight of the shell, also presents a source of difficulty.

The fallibility of even the most simple forms of fuze, manufactured in very large numbers, although it may be remote, must always engender a feeling of insecurity, when shells are employed containing an explosive agent of the class which, in recent years, it has been sought, by every resource of ingenuity, combined with intimate knowledge of the properties of these explosives, to apply as substitutes for gunpowder in shells, on account of their comparatively great destructive power.

One of the first uses, for purposes of warfare, to which it was attempted to apply gun-cotton, was as a charge for shells. But even when this was highly-compressed, and accurately fitted the shell chamber, with the intervention only of a soft packing between the surfaces of explosive and of metal, to guard against friction between the two upon the shock of the discharge, no security was attainable against the ignition of the comparatively sensitive explosive by friction established within its mass at the moment when the shell is first set in motion. By the premature explosion of a shell charged with gunpowder, no important injury is inflicted upon the gun, but a similar accidental ignition of a gun-cotton charge must almost inevitably burst the arm. The earlier attempts to apply gun-cotton as a bursting-charge for shells were several times attended by very disastrous accidents of this kind; but the fact, afterwards discovered, that wet compressed gun-cotton, even when containing sufficient water to render it quite unflammable, can be detonated through the agency of a sufficiently powerful charge of fulminate of mercury, or of a small quantity of dry gun-cotton, imbedded within it, has led to the perfectly safe application of gun-cotton in shells, provided the fuze, through the agency of which the initiative detonating agent in the shell comes into operation, is secure against any liability to premature ignition when the gun is fired. Many successful experiments have been made with shells thus charged with wet gun-cotton, which is now recognised as a formidable destructive agent applicable in shells with much less risk of casualty than attends the use of many other of the violent explosive bodies which it has become fashionable, in professional parlance, to designate as "high explosives."

Many devices and arrangements, more or less ingenious and complicated, have been schemed, especially in the United States, for applying preparations of the very sensitive liquid, nitro-glycerin, such as dynamite and blasting-gelatin, as charges for shells. Some of these consist in subdividing the charge by more or less elaborate methods; in others the shell is also lined with some soft elastic packing material, and paddings of similar material are applied in the head and the base of the shell-chamber, with the object of reducing the friction and concussion to which the explosive is exposed when the projectile is first set in motion. Such arrangements obviously reduce the space available for the charge in the shell, and the best of them fail to render these explosives as safe to employ as wet gun-cotton. In order to avoid exposing shells loaded with such explosives to the concussion produced when propelling them by a powder-charge, compressed air has been applied as the propelling agent, and guns of special construction and very large dimensions, from which shells containing as much as 500 lbs. of gun-cotton or dynamite are projected through the agency of compressed air, have recently been elaborated in the United States, where great expectations are entertained of the value, for war purposes, of these so-called pneumatic guns.

A highly ingenious device for utilising a class of very powerful explosives in shells, without any risk of accident to the gun, was not long since brought forward by Mr. Grusen, the well-known armour-plate and projectile manufacturer of Magdeburg. It consisted of a thoroughly efficient arrangement for applying the fact, first demon-

strated by Dr. Sprengel, that mixtures of nitric acid of high specific gravity with solid or liquid hydrocarbons, or with the nitro-compounds of these, are susceptible of detonation, with development of very high energy. The two agents, of themselves non-explosive—nitric acid and the hydro-carbon, or its nitro product—are separately confined in the shell; when it is first set in motion by the firing of the gun, the fracture of the receptacle containing the liquid nitric acid is determined by a very simple device; the two substances are then free to come into contact, and their very rapid mixture is promoted by the rotation of the shell, so that almost by the time that it is projected from the gun, its contents, at first quite harmless, have become converted into a powerfully explosive mixture, ready to come into operation through the action of the fuze. Although safety appears assured by this system, the comparatively complicated nature of the contrivance, and the loss of space in the shell thereby entailed, place it at a disadvantage, especially since some other very violent explosive agents have come to be applied with comparative safety in shells.

Between four and five years ago intelligence first reached us of marvellously destructive effects produced by shells charged with an explosive agent which the French Government was elaborating. The reported results surpassed any previously recorded in regard to violently destructive effects and great velocity of projection of the fragments of exploded shells, and it was asserted that the employment of this new material, Mélinite, was unattended by the usual dangers incident to this particular application of violent explosive agents, an assertion scarcely consistent with accounts which soon reached us of several terrible calamities due to the accidental explosion of shells loaded with Mélinite.

Although the secret of the precise nature of Mélinite has been extremely well preserved, it transpired ere long that extensive purchases were made in England, by or for the French authorities, of one of the many coal-tar derivatives which for some years past has been extensively manufactured for tinctorial purposes, but which, although not itself classed among explosive bodies until quite lately, had long before been known to furnish, with some metals, more or less highly explosive combinations, some of which have been applied to the production of preparations suggested as substitutes for gunpowder.

The product of destructive distillation of coal from which, by oxidation, this material is now manufactured, is the important and universally-known antiseptic and disinfectant, carbolic acid, or phenol. Originally designated carbazotic acid, the substance now known as picric acid was first obtained in small quantities as a chemical curiosity by the oxidation of silk, aloes, &c., and of the well-known blue dye indigo, which thus yielded another dye of a brilliant yellow colour. To the many who may regard this interesting phenol-derivative as a material concerning the stability and other properties of which we have little knowledge, it will be interesting to learn that it has been known to chemists for more than a century. It was first manufactured in England for tinctorial purposes by the oxidation of a yellow resin (*Xanthorrhoea hastilis*), known as Botany Bay gum. Its production from carbolic acid was developed in Manchester in 1862, and its application as a dye gradually extended, until, in 1886, nearly 100 tons were produced in England and Wales.

Although picric acid compounds were long since experimented with as explosive agents, it was not until a very serious accident occurred, in 1887, at some works near Manchester where the dye had been for some time manufactured, that public attention was directed in England to the powerfully explosive nature of this substance itself. The French authorities appear, however, to have been at that time already engaged upon its application as an explosive for shells. It is now produced in very large quantities at several works in Great Britain, and it has been exten-

ively exported during the last four years, evidently for other than the usual commercial purposes. Large supplies of phenol, or carboic acid, have, at the same time, been purchased in England for France, and lately for Germany, doubtless for the manufacture of picric acid, very extensive works having been established for its production in both those countries. It has been made the subject of experiment by our military authorities, and its position has been well established as a thoroughly stable explosive agent, easily manufactured, comparatively safe to deal with, and very destructive when the conditions essential for its detonation are fulfilled.

The precise nature of Mélinite appears to be still only known to the French authorities: it is asserted to be a mixture of picric acid with some material imparting to it greater power; but accounts of accidents which have occurred even quite recently in the handling of shells charged with that material appear to show that, in point of safety or stability, it is decidedly inferior to simple picric acid. Reliable as the latter is, in this respect, its employment is, however, not unattended with the difficulties and risks which have to be encountered in the use, in shells, of other especially violent explosives. Future experience in actual warfare can alone determine decisively the relative value of violent explosive agents, like picric acid or wet gun-cotton, and of the comparatively slow explosive, gunpowder, for use in shells; it is certain, however, that the latter still presents distinct advantages in some directions, and that there is no present prospect of its being more than partially superseded as an explosive for shells.

With regard to submarine mines and locomotive torpedoes, such as those marvels of ingenuity and constructive skill, the Whitehead and Brennan torpedoes, the important progress recently made in the practical development of explosive agents has not resulted in the provision of a material which equals wet compressed gun-cotton in combining with great destructive power the all-important essential of safety to those who have to deal with these formidable weapons and to man the small vessels which have to perform the very hazardous service of attacking ships of war at short distances by means of locomotive torpedoes.

Although the subject of the development of explosive force for purposes of war has of late received from workers in applied science, from seekers of patentable inventions, and even from the public generally, a somewhat predominating share of attention, considering that we congratulate ourselves upon the enjoyment of a period of profound peace, yet the production of new explosive agents for mining and quarrying purposes, which present or lay claim to points of superiority over the well-established blasting agents, has been by no means at a standstill. For many years the main object sought to be achieved in this direction was to surpass, in power or adaptability to particular classes of work, the well-known preparations of nitroglycerin and gun-cotton, which, during the past twenty years, have been formidable competitors and, in many directions, absolutely successful rivals of black powder. It is both interesting and satisfactory to note, however, that this object has of late, and especially since the publication of the results of labours of English and foreign Commissions on the causes of mine accidents, been prominently associated with endeavours to solve the important problems of combining, in an explosive agent, efficiency in point of power with comparative non-sensitiveness to explosion by friction or percussion, and of securing its effective operation with little or no accompaniment of projected flame. Safety-dynamites, flameless explosives, water-cartridges, and other classes of materials and devices connected with the getting of coal, the quarrying of rock, or the blasting of minerals, have claimed the attention of those who guide the miner's work; in some of these directions the practical results obtained have been beyond question important,

and, indeed, conclusive as regards the great diminution of risks to which men need be exposed in those coal mines where the ordinary use of explosives, although not altogether inadmissible, may at times be attended with danger. It is to be feared that those results are still far from receiving the amount of application which might reasonably be hoped for; but, at any rate, there are, among the extensive mining districts where the employment of explosives in connection with the getting of coal cannot be dispensed with, several of importance where the use of gunpowder has almost entirely given place to the adoption of blasting-agents or methods of blasting, the employment of which is either not, or only very exceptionally, attended by the projection of flame or incandescent matter into the air where the shot is fired.

The mining public is especially indebted to German workers for much of the success which has been obtained in this direction, and also to the eminent French authorities, Mallard and Le Chatelier, for their thorough theoretical and practical investigations bearing upon the prevention of accidental ignition of fire-damp during blasting operations. Having arrived at the conclusion that fire-damp and air-mixtures are not ignited by the firing of explosive preparations which develop by their detonation temperatures lower than 2220° C., they found that ammonium nitrate, although in itself susceptible of detonation, does not develop a higher temperature than 1130° C., while the temperature of detonation of nitroglycerin and gun-cotton are, respectively, 3170° and 2636°. The admixture of that salt with nitroglycerin or gun-cotton in sufficient proportion to reduce the temperature of detonation to within safe limits allows, therefore, of the employment of those explosive agents in the presence of fire-damp mixtures without risk of accident, and this fact has led to the effective use of such mixtures as safe blasting agents in coal.

Those who have been content to labour long and arduously with the objects steadily in view of advancing our knowledge of the causes of mine accidents and of developing resources and measures for removing or combating those causes, can cherish the conviction that recent improved legislation in connection with coal mines, based upon the results of those labours, has been already productive of decided benefits to the miner, even although it has fallen short of what might reasonably have been hoped for as an outcome of the very definite results and conclusions arrived at by the late Royal Commission on Accidents in Mines (in the recent much-lamented death of whose universally respected chairman, my late esteemed friend and colleague, Sir Warrington Smyth, the scientific world has sustained the loss of an ardent worker, and the miner of an invaluable friend).

The fearful dangers arising from the accumulation of inflammable dust in coal mines, and the equality of mine dust with fire-damp in its direful power of propagating explosions, which may sometimes even be, in the first instance, established chiefly or entirely through its agency, have now been long recognised as beyond dispute; and it is satisfactory to know that permission to fire shots in mine workings which are dry and dusty has, by recent legislation, been made conditional upon the previous laying of the dust by effective watering. In some mining districts, moreover, the purely voluntary practice has been extensively adopted by mine-owners of periodically watering the main roads in dry and dusty mines, or of frequently discharging water-spray into the air in such roads, which must tend greatly to reduce the possible magnitude of the disastrous results of a fire-damp or dust-explosion in any part of the mine workings.

The encouragement given to the application of the combined resources of ingenuity, mechanical skill, and knowledge of scientific principles, through the elaborate, but thoroughly practical comparative trials to which almost every variety of safety lamp has, during the last few years, been submitted by competent and conscientious experimenters, has resulted in the provision of lamps to

the hand of the miner which combine the essential qualities of safety, under the most exceptionally severe conditions, with good illuminating power, simplicity of construction, lightness, and moderate cost. Very important progress has also been made, since the first appointment of the late Accidents in Mines Commission, towards the provision of thoroughly serviceable and safe portable electric lamps for use in mines. Of those which have already been in the hands of the miners, several have fairly fulfilled his requirements as regards size, weight, and illuminating power of sufficient duration; but much still remains to be accomplished with respect to durability, simplicity, thorough portability, and cost, before the self-contained electric lamp can be expected to compete successfully with the greatly improved miners' lamps which are now in use, or available.

The recent legislation in connection with mines is certainly deficient in any sufficiently decisive measure for excluding from mine workings certain forms of lamps which, while fairly safe in the old days of sluggish ventilation, are unsafe in the rapid air-currents now frequently met with in mines; it is, however, very satisfactory to know that the strong representations on this subject, made by the late Commission, combined with force of example and with the conclusive demonstration of the superiority of other lamps, by exhaustive experiments, have led within the last two years to the very general abandonment of the unprotected Davy, Clanny, and Stephenson lamps in favour, either of simple, safe, modifications of these, or of other safe and efficient lamps, and that one possible element of danger to the miner has thus been eliminated, at any rate in many districts. In one important respect recent improved legislation has failed to effect a most desirable change—namely, in the substitution of safety lamps for naked lights in workings where small local accumulations of fire-damp are discovered from time to time. There appears little doubt that one of the three fearful explosions which have occurred within the last twelve months—the explosion at Llanerch Colliery, near Pontypool—was caused by the continued employment of naked lights in a mine where inspection constantly revealed the presence of fire-damp. This explosion, and two other terrible disasters, at Mossfield Colliery, in Staffordshire, and at Morfa Colliery, near Swansea, which have occurred since the last meeting of the Association, may have seemed to weaken the belief that the operation of the recent Mines Regulation Act, which was based upon some of the results of seven years' arduous labour of the late Mines' Commission, must have resulted in very substantial improvement in the management of mines and in the conduct of work by the men. Happily, however, there is a consensus of opinion among those most competent to judge—i.e., the Government Mine Inspectors—that very decided benefits have already accrued from the operation of the new Act. Although far from embodying all that the experienced mine owners, miners, and scientific workers upon that Commission, as well as practical authorities in Parliament, concurred in regarding as reasonably adaptable, from the results of observation and experiment, to the furtherance of the safer working of mines, this Act does include measures, precautionary and preventive, of undeniable utility, well calculated to lessen the dangers which surround the miner, and to add to his personal comfort underground. We may hope, moreover, that the operation of the Act is paving the way to more comprehensive legislation in the near future; for it can scarcely be doubted by the light of recent sad experience, that there are indications in which both masters and men still hesitate to adopt, of their own free will, measures or regulations, methods of working or appliances and precautions, which are calculated to be important additional safeguards against mine accidents, and which are either left untouched, or only hesitatingly and imperfectly dealt with in the recent enactments.

My labours upon the late Mines' Commission represent

only one of several subjects in connection with which it has been my good fortune to have opportunities of rendering some slight public service in directions contrasting with one of the main functions of my career, by endeavouring to apply the results of scientific research to a diminution of the risks to which particular classes of the community, or the public at large, are exposed—of being sufferers by explosions, the results of accidents or other causes.

During the pursuit of bread-winning vocations, and even in ordinary domestic life, the conditions, as well as the materials, requisite for determining more or less disastrous explosions are often ready to hand, and their activity may be evoked at any moment through individual heedlessness or through pure accident. Steam, or gases confined under pressure, volatile inflammable liquids, combustible gases, or finely-divided inflammable solids, are now all well recognised as capable of assuming the character of formidable explosive agents; but with respect to the three last named, it is only of late that material progress has been made towards a popular comprehension and appreciation of the conditions conducive to danger, and of those by the fulfilment of which danger may be avoided. Thus, the causes of explosions in coal-laden ships, together with the occurrence of spontaneous ignition in coal cargoes, another fruitful source of disaster, were made the subject of careful inquiry some years ago by a Royal Commission, upon which I had the pleasure of working with the late Dr. Percy, whose invaluable labours for the advancement of metallurgic science will always be gratefully remembered. The light thrown by that inquiry upon the causes of those disasters, and upon the conditions to be fulfilled for guarding against the accumulations of fire-damp, gradually escaping from occlusion in coal, and of heat, developed by chemical changes occurring in coal cargoes, has unquestionably led to an important reduction of the risks to which coal-laden ships are exposed. Subsequent official inquiries and experimental investigations, in which I took part with the late Sir Warrington Smyth and other eminent naval officers, consequent upon the loss of H.M.S. *Doterel* through the accidental ignition of an explosive mixture of petroleum spirit-vapour and air (and other calamities in warships originating with the gradual emission of fire-damp from coal), have resulted in the adoption of efficient arrangements for ventilating all spaces occupied by, and contiguous to, the large supplies of fuel which these vessels have to carry.

The thorough investigation, by Rankine and others, of the causes of explosions in flour mills, which in years past were so frequent and disastrous, has secured the adoption of efficient measures for diminishing the production, and the dissemination through channels and other spaces in the mills, of explosive mixtures of flour-dust and air, and for guarding against their accidental ignition. The numerous terrible accidents caused by the formation and accidental ignition of explosive mixtures of inflammable vapour and air in ships carrying cargoes of petroleum stored in barrels or in tanks, have, by the investigations to which they have given rise, led to the indication of effective precautionary measures for guarding against their recurrence. Again, the many distressing accidents, frequently fatal, which have attended the domestic use of those valuable illuminants, petroleum and mineral oils of kindred character, have been made the subject of exhaustive investigations, which have demonstrated that these disasters may readily be prevented by the employment of lamps of proper construction, and by the observance of very simple precautions by the users of them; and a recent official inquiry which I have conducted with Mr. Boverton Redwood has furnished most gratifying proof that very substantial progress has been made within the last few years by lamp manufacturers in the voluntary adoption of such principles of construction as we had experimentally demonstrated to be essential for securing the safe use of mineral oils in lamps for lighting and heating purposes, the employment of which has,

within a brief period, received enormous extension in this and other countries.

The creation and rapid development of the petroleum industry has, indeed, furnished one of the most remarkable illustrations which can be cited of industrial progress during the period which has elapsed since the British Association last met in Leeds. One year after that meeting—viz., on August 28, 1859, the first well, drilled in the United States with the object of obtaining petroleum, was successfully completed, and the rate of increase in production in the Pennsylvania oil-fields during the succeeding years is shown by the following figures:—

In 1859, 5000 barrels (of forty-two American gallons) were produced. In the following year the production increased to 500,000 barrels; while in the next year (1861) it exceeded 2,000,000 barrels, at which figure it remained, with slight fluctuations, until 1865. The supply then continued to increase gradually, until, in 1870, it reached nearly 6,000,000 barrels; while in 1874 it amounted to nearly 11,000,000 barrels. In 1880 it amounted to over 26,000,000 barrels, and in 1882 it reached 31,000,000. Since then the supply furnished by the United States has fallen somewhat, and last year it amounted to 21,500,000 barrels. The production of crude petroleum in the Pennsylvania fields, large as it has been, has not, however, kept pace with the consumption, for we find that the accumulated stocks, which on December 31, 1888, amounted to over 18,000,000 barrels, had become reduced to about 11,000,000 barrels at the close of last year. At this rate the surplus stock above ground will have vanished by the end of the current year. In addition to the petroleum raised in Pennsylvania, there is now a very large production in the State of Ohio; but this has not as yet been employed as a source of lamp-oil; it is, however, transported by pipe line in great quantities to Chicago, for use as liquid fuel in industrial operations.

A few years after the development of the United States petroleum industry, the production of crude petroleum in Russia also began to extend very rapidly. For more than 2500 years Baku, on the borders of the Caspian Sea, has been celebrated for its naphtha springs and for the perpetual flames of the Fire Worshippers, fed by the marvellous subterranean supplies of natural gas. To a limited extent neighbouring nations appear to have availed themselves of the vast supplies of mineral oil at Baku during the past one thousand years. By the thirteenth century the export of the crude oil had already become somewhat extensive, but the production of petroleum from it by distillation is of comparatively recent date. In 1863 the supplies of petroleum from the Baku district amounted to 5018 tons; they increased to somewhat more than double during the succeeding five years. In 1869 and following three years the production reached about 27,000 tons annually, and in 1873 it was about 64,000 tons; three years later, 153,000 tons were produced, and in the following five years there was a steady annual increase, until, in 1882, the production amounted to 677,269 tons; in 1884 it considerably exceeded 1,000,000 tons, and last year it had reached the figure of about 3,300,000 tons. The consumption of crude petroleum as fuel for locomotive purposes has, moreover, now assumed very large proportions in Russia, and many millions of gallons are annually consumed in working the vast system of railways on both sides of the Caspian Sea.

The imported refined petroleum used in this country in lamps for lighting, heating, and cooking, was exclusively American until within the last few years, but a very large proportion of present supplies comes from Russia. The imports of kerosene into London and the chief ports of the United Kingdom during 1889 amounted to 1,116,205 barrels of United States oil, and 771,227 barrels of Russian oil. During the same period the out-turn of mineral oil for use in lamps by the Scottish Shale Oil Companies probably amounted to about 500,000 barrels.

Another important feature connected with the development of the petroleum industry is the great extent to

which the less volatile products of its distillation have replaced vegetable and animal oils and fats for lubricating purposes in this and other countries. The value of petroleum as a liquid fuel and as a source of gas for illuminating purposes has, moreover, been long since recognised, as it is probable that one outcome of the attention which is now being given to the hitherto unworked deposits of petroleum in the East and West Indies, South America, and elsewhere, will be a very large increase in its application to these purposes. In the East Indies there are vast tracts of oil-fields in Burmah, Baluchistan, Assam, and the Punjab. The native Rangoon oil industry is one of great antiquity, although the oil was only used in the crude condition until about thirty-five years ago, at which time Dr. Hugo Müller, with the late Warren De la Rue, whose many sided labours and generous benefactions have so importantly contributed to the advancement of science, made valuable researches on the products furnished by crude oil imported from Rangoon. The resources of the oil-fields of Upper Burmah, especially of the district of Yenangyoung (or *crack of stinking water*), have since then been developed by British enterprise, and have attained to considerable importance since our annexation of Upper Burmah.

The great extension of the petroleum trade is gradually leading to very important improvements in the system of transport of the material over water and on land. Until recently this has been carried out entirely in barrels and tin cases; the consequent great loss from leakage and evaporation, accompanied by risk of accident, is now becoming much reduced by the rapidly increasing employment of tank steamers, which transport the oil in bulk. Tank railway wagons have for some time past been in use in Russia, and there is prospect of these and of tank barges being adopted here for the distribution of the oil; while in London, the practice is already spreading gradually of distributing supplies to tradesmen from tank road wagons. Some considerable doubt as to whether the risk of accident has not rather been altered in character than actually reduced by the new system of transport, has not unnaturally been engendered in the public mind by the occurrence within a comparatively short period of several serious disasters during the discharge of cargoes from tank vessels. The memorable explosion which took place in October, 1888, on board the *Ville de Calais*, in Calais Harbour, with widespread, destructive effects, was followed by a similarly serious explosion in the *Ferguson*, at Rouen, last December, and, more recently, by a fire of somewhat destructive character at Sunderland, resulting from the discharge into the river of petroleum residues from a ship's tanks. In all these cases the petroleum was of a nature to allow inflammable vapour to escape readily from the liquid, so that an explosive mixture could be rapidly formed by its copious diffusion through the air. No similar casualty has been brought to notice as having happened to tank ships carrying petroleum oil of which the volatility is in accordance with our legal requirements, and this points to the prudence of restricting the application of the tank system to the transport and distribution of such petroleum as complies with well-established conditions of safety.

Another most remarkable feature connected with the development of the petroleum industry is presented by the utilisation within the last few years of the vast supplies of natural inflammable gas furnished by the oil-fields.

In America this remarkable gas supply was for a long time only used locally, but before the close of 1885 its conveyance to a distance by pipes, for illuminating and heating purposes, had assumed large proportions, one of the companies in Pittsburgh having alone laid 335 miles of pipes of various sizes, through which gas was supplied equivalent in heating value to 3,650,000 tons of coal per annum. Since then the consumption in and around Pittsburgh has probably been at least tripled. At the close of 1886 six different companies were conveying

natural gas by pipes to Pittsburgh from 107 wells; 500 miles of pipe ranging in diameter from 30 inches to 3 inches, were used by these companies, 232 miles of which were laid within Pittsburgh itself. The Philadelphia Company, the most important of these associations, then owned the gas supply from 54,000 acres of land situated on all the anti-clinals around Pittsburgh, but drew its supplies only from Tarentum and the Murraryville field. It supplied, in 1886, 470 factories and about 5000 dwellings within the city, besides many factories and dwellings in Alleghany, and in numerous neighbouring villages. The average gas pressure at the wells, when the escape is shut off, is about 500 lbs. per square inch, and in the case of new wells this pressure is very greatly exceeded. In order to minimise the danger from leakage, the gas-pressure in the city is reduced to a maximum of 13 lbs., and is regulated by valves at a number of stations under the control of a central station. The usual pressure in the larger lines is from 6 to 8 lbs., while in the low pressure lines it does not exceed 4 to 5 ounces.

The effect of the change from coal gas to natural gas upon the atmosphere over Pittsburgh has been most marked: formerly the sky was constantly obscured by a canopy of dense smoke; now the atmosphere is clear, and even white paint may with impunity be employed for the house fronts.

The very rapid development of the employment of natural gas is not confined to the neighbourhood of Pittsburgh; it is used for heating purposes in the cities of Buffalo, Erie, Jamestown, Warren, Olean, Bradford, Oil City, Titusville, Meadville, Youngstown, and perhaps twenty more towns and villages in Pennsylvania and North-Western New York. In North-Western Ohio, the cities of Toledo and Sandusky, the towns of Findlay, Lima, Tiffin, Fostoria, and others in that section are also supplied with natural gas; a pipe line has moreover been recently laid to Detroit, Mich., and it is estimated that in these localities 36,131,669,000 cubic feet of the gas were consumed during last year, displacing 1,802,500 tons of coal. To the south-west of Pittsburgh there are many smaller places which consume natural gas; it also occurs in considerable quantity, and is being utilised, in Indiana (whence an account has recently reached us of a terrific subterranean explosion of the gas); and it is at the present time contemplated to carry a natural gas supply to Chicago.

The utilisation of the natural gas of the Russian oil fields, although of a very ancient date, has hitherto not been extensive, neither does the magnitude of the supply appear to bear comparison with that of the Pennsylvanian district.

A form of gaseous fuel which has long been known to technical chemists and metallurgists, but which has of late attracted considerable attention, especially in connection with the recent interesting work relating to its applications pursued by Mr. Samson Fox, of Leeds, has become, within the last four years, a competitor in the United States, both of the natural gas of Pennsylvania and of coal gas. Since Felix Fontana first produced so-called water-gas in 1780, by passing vapour of water over highly heated fuel, many methods, differing chiefly in small details, have been proposed for carrying out the operation, with a view to the ready and cheap production of the resulting mixture of hydrogen and carbonic oxide, and numerous technical applications of water-gas have been suggested from time to time, with no very important results, excepting as regards its use for lighting purposes. Being of itself non-luminous, its utilisation in this direction is accomplished, either by mixing it with a highly luminous gas, or by causing a hydrocarbon vapour to be diffused through it, or the non-luminous flame, produced by burning it in the air, is made to raise to incandescence some suitably prepared solid substance, such as magnesia, lime, a zirconium salt, or platinum, whereby bright light is emitted. The objection to its employment as an illuminant for use in buildings,

to which great weight is attached by us, and rightly, as sad experience has shown—viz., that, as it consists, to the extent of about one-half its volume, of the highly poisonous gas carbonic oxide, the atmosphere in a confined space may be rendered irrespirable by a small accidental contamination with water-gas, by leakage or otherwise, not detectable by any odour—appears to constitute no great impediment to its employment in the United States, as it is now manufactured for illuminating and heating purposes by a large proportion of their gasworks, being in some places employed in admixture with a highly luminous coal-gas, in others rendered luminous by the alternative methods mentioned. It is stated that about three-fourths of the illuminating gas now supplied to the cities of New York, Brooklyn, Philadelphia, Jersey, St. Paul, and Minneapolis, is carburetted water gas; in Chicago the entire supply now consists of this gas, and Boston will also soon be supplied exclusively with it. The use of water-gas for metallurgic work does not appear to be contemplated in the United States, but it is especially to such applications of the gas that much attention has been devoted here in Leeds; and although some eminent experts are sceptical regarding the attainment of advantages, especially from an economical point of view, by the employment of this form of gaseous fuel, especially after practical experience in the same direction acquired in Germany, the technical world must feel grateful to Mr. Fox for his work in this direction, affording, as it does, an interesting illustration of the qualities of perseverance and energy which, when combined with sound knowledge, often achieve success in directions that have long appeared most unpromising—qualities which have been characteristic of many pioneers in industrial progress in this country.

Leeds has been especially fortunate in the possession of such pioneers who, when competition brought about great changes in the particular trade through which, for many generations, this city chiefly enjoyed prosperity and high renown, developed its power and resources in new directions, from which success soon flowed in continually increasing measure. The rapid rise of Leeds to its present high position in industrial prosperity and national importance most probably dates from the period when its chief staple industry began to experience serious rivalry, in its own peculiar achievements, on the part of other districts of the kingdom and of other countries. From early days a flourishing Centre of one of the provinces of Great Britain most richly endowed with some of Nature's best treasures, Leeds could scarcely have failed, through the energy, acute intelligence, and powerful self-reliance especially characteristic of the men of Yorkshire, to rapidly acquire fresh renown in connection with industries which either were new to the town and district, or had been pursued in comparatively modest fashion, and which have combined to place the Leeds of to day upon a higher pinnacle of commercial prosperity, power, and influence than her patriotic citizens of old could ever have dreamt of.

An examination into the present educational resources of Leeds places beyond any doubt the fact that her present prosperity in commerce and industries is in no small degree ascribable to the paramount importance long since attached here to the liberal provision of facilities for the diffusion of knowledge among the artisan and industrial classes, and especially for the acquisition of a sound acquaintance with the principles of the sciences and their applications to technical purposes, with particular reference to the prominent local industries, by all grades of those who pursue or intend to pursue them. There is, probably, no town in the kingdom more amply provided with efficient elementary and advanced schools for both sexes, while the special requirements of the artisan are efficiently met by the prosperous School of Science and Technology. The resources of the Yorkshire College provide, in addition a combination of thorough scientific education with really practical training in the more

important local industries; indeed, during the sixteen years of its continually progressive work, this institution has acquired so widespread a reputation that students come from abroad to reap the advantages afforded by the unrivalled textile and dyeing departments of the Leeds College. The keen competition now existing between these departments and the corresponding branches of the much younger but most vigorous sister College at Bradford, can only conduce to the further development of both, and to their thorough maintenance up to the requirements of the day.

The very important pecuniary aid afforded to these establishments, and to a number of other technical schools in Yorkshire, by one of the most important of the ancient companies of the City of London, the Clothworkers, affords an interesting illustration of the good work in the cause of education performed by those Guilds and, especially of late years, by means of their flourishing Institute for the advancement of technical education which, through its two great instructional establishments in London, and through the operation of its system of examinations throughout the country, extending now even to the Colonies, has afforded very important aid towards eradicating the one great blot upon our national educational organisation. To have been first in the field in practically developing a far-reaching scheme for the advancement of technical education in this country must continue to be a source of pride to the City of London and its ancient Guilds in time to come, when the operation of efficient legislation, supported and extended by patriotic munificence and by the hearty co-operation of associations of earnest and competent workers in the cause, shall have placed the machinery and resources for the technical instruction of the people upon a footing commensurate with our position among Nations.

The remarkable Address delivered by Owen here in 1858, wherein the condition, at that time, of those branches of natural science which he had made particularly his own was most comprehensively reviewed, included some specially interesting observations on the importance to the cultivation and progress of the natural sciences, and to the advancement of education of the masses of this country, of providing adequate space and resources for the proper development of our National Museum of Natural History; and it cannot but be a source of great satisfaction and pride to him to have lived to witness the thoroughly successful realisation of the objects of his own indefatigable strivings and powerful advocacy in that direction. Comprehensive as were the views adopted by Owen regarding the scope and possible extension of that museum, it may, however, be doubted whether they ever embraced so extensive a field as was presented for our contemplation by his successor last year, when he told us that a natural history museum should, in its widest and truest sense, represent so far as they can be illustrated by museum specimens, all the sciences which deal with natural phenomena, and that the difficulties of fitly illustrating them have probably alone excluded such subjects as astronomy, physics, chemistry, and physiology, from occupying departments in our National Museum of Natural History.

The application, in its broadest signification, of the title Natural History Museum may doubtless be considered to include, not only illustrations and examples of the marvellous works of the Creator and of the results of man's labours in tracing their intimate history and their relations to each other, but also illustrations of the means employed, and of the results attained, by man in his strivings to fathom and unravel the laws by which the domains of Nature are governed. But, the reason why representative collections, illustrative of the physical sciences, do not form part of our National Natural History Museum, has, I venture to think, scarcely been correctly ascribable to any difficulty of organising fit illustrations of methods of investigation, of the attendant

appliances, and of the results attained by experimental research; it appears rather to exist in the fact that physical science has hitherto had no share in such a combination of circumstances as has been favourable to the good fortunes and advancement of the natural sciences, and is analogous to those which, from time to time, give rise to the provision of increased accommodation for our National Art Treasures. Our present National Science Collection, which has, indeed, had a struggle for existence, does not owe the development it has hitherto experienced to any such moral pressure as has been several times exercised in the case of our art collections, by the munificence of individuals, with the result of securing substantial aid from national resources; its gradual increase in importance has been due to the untiring perseverance of men of science, and of a few prominent influential and public spirited authorities, in keeping before the public the lessons taught by careful inquiries, such as those entrusted to the Royal Commission on Scientific Instruction, into the opportunities afforded for the cultivation of science and the development of its applications, in other countries, as compared with those provided here.

The success of the efforts made in 1875 by a committee thoroughly representative of every branch of experimental science to bring together in London an international loan collection of scientific apparatus, and the widespread interest excited by that collection, led the President of the Royal Society, in union with many distinguished representatives of science, to lay before our Department of Education a proposal to establish a national museum of pure and applied science, including the Museum of Inventions, which had already existed since 1860 as a nucleus of a science museum, the establishment whereof had formed part of the original scheme of the Science and Art Department. The Loan Collection of 1876 did, in fact, and in consequence of the urgent representations then made, first put into practical shape the long cherished desire of men of science to see an Institution arise in England similar to the Conservatoire des Arts et Métiers of France, and it became the starting point of the National Collection representative of the several branches of experimental science, which has been undergoing slow but steady development since that time, patiently awaiting the provision of a suitable home for its contents. This collection, which illustrates not only the means whereby the triumphs of scientific research have been and are achieved, but also the methods by which these departments of science are taught, yields, small as it is, to none of our national museum treasures in interest and importance.

In yet another way did that Loan Collection become illustrious: one of the most interesting features connected with it was the organisation of a series of important conferences and explanatory lectures, serving to illustrate, and also greatly to enhance, its value, and affording most invaluable demonstration of the way in which such collections must exercise direct influence upon the advancement of science and upon the diffusion of scientific knowledge. These lectures and conferences demonstrated the wisdom of the suggestion made by the illustrious representative of associated Science in Leeds eighteen years previously, that public access to museums should be combined with the delivery of lectures emphasising and amplifying the information afforded by their contents. The example there set of thoroughly utilising for instructional purposes, and for the advancement of science, a collection illustrative of the physical sciences, has since been followed by the Science and Art Department; illustrative lectures connected with the existing nucleus of a national science collection therewith have been delivered from time to time, and the objects in the collection are constantly utilised in the courses of instruction of the adjoining Normal School of Science.

Although the national importance of thoroughly representative and continuously maintained science

collections has long been manifest, not only to all workers in science, but also to all who have cared to enquire, even superficially, into the influence of the cultivation of science upon the industrial and commercial prosperity of the country, the labours of a Royal Commission and of successive Committees, in demonstrating the necessity for the provision of adequate accommodation for such collections, and for their support upon the basis of that afforded to the natural history collections, have been very long in bearing fruit. However, lovers of science, and those who have the prosperity of the country near at heart, have at length cause for rejoicing at the acquisition by the Nation of a site in all respects suitable and adequate for the accommodation of the science collections, which, as soon as appropriate buildings are provided for their reception, will not fail, in comprehensiveness and completeness, to become worthy of a Country which has been the birthplace of many of the most important discoveries in science, and of a People who have led the van among all Nations in making the achievements of science subservient to the advancement of industries and commerce.

The site selected as the permanent home of our National Science Collections is immediately in rear of the Natural History Museum, and faces the stately edifice, now rapidly progressing towards completion, for the erection of which, as an Imperial memorial of the Queen's Jubilee, funds were provided by voluntary contributions from every portion of the Empire and every class in the Empire's Nations. The Imperial Institute, the conception of which we owe to His Royal Highness the Prince of Wales, occupies a central position among buildings devoted to the illustration and cultivation of pure and applied Science and of the Arts—i.e., the Normal School of Science, the Technical College of the City and Guilds of London, the National Schools of Art, the Science Museum, the South Kensington Museum, and the Royal College of Music; to which we may ere long see added a National Gallery of representative British Art. A more fitting location could scarcely be conceived for this pre-eminently National Institution, which has for its main objects the comprehensive and continuously progressive illustration: of the practical applications of the vast resources presented by the Animal, Vegetable, and Mineral Kingdoms to Industries and the Arts; of the extent and the progressive opening of those resources in all parts of the Empire; of the practical achievements emanating from the results of scientific research; and of the utilisation of the Arts for the purposes of daily life. With the attainment of these objects it will be the function of the Imperial Institute to combine the continuous elaboration of systematic measures tending to stimulate progress in trades and handicrafts, and to foster a spirit of emulation among the artizan and industrial classes. Another branch of the Institute's work, upon which it is already engaged, is the systematic collection of data relating to the natural history, commercial geography, and resources of every part of the empire, for wide dissemination together with all current information, bearing upon the commerce and industries of the Empire and of other Countries, which can be comprised under the head of Commercial Intelligence. The achievement of these objects should obviously tend to maintain intimate intercourse, relationship, and co-operation between the great Home and Colonial centres of Commerce, Industries, and Education, and to enhance importantly our power of competing successfully in the great struggle, in which Nations are continuously engaged, for supremacy in commercial and industrial enterprise and prosperity.

To the elaboration of the practical details of a system of operation calculated to secure the objects I have indicated, eminent public spirited men are now devoting their best energies, with the sanguine expectation of realising the hope cherished by the Royal Founder of the Imperial Institute, that this memorial of the completion, by our beloved Sovereign, of fifty years of a wise and

prosperous reign, is destined to be one of the most important bulwarks of this County, its Colonies and Dependencies, by becoming a great centre of operations, ceaselessly active in fostering the unity, and developing the resources, and thus maintaining and increasing the power and prosperity, of our Empire.

CORRESPONDENCE.

ELECTRO-DEPOSITION OF SILVER.

To the Editor of the Chemical News.

SIR,—I had occasion recently to prepare a conducting surface on plaster casts for coating with copper by electrical deposit; the ordinary method of obtaining a deposit of finely-divided silver seemed rather lengthy, especially as it necessitated soaking the cast in wax. A good deposit of silver may be obtained by a somewhat simpler mode of procedure if the cast be moistened with water and brushed over with a solution of silver nitrate; it is then allowed to come into contact with antimoniretted or arseniuretted hydrogen, which can readily be prepared by adding compounds of antimony or arsenic to a flask in which hydrogen is being evolved from lime and dilute sulphuric acid. An instant deposit of Ag_3Sb occurs, which is an excellent conductor.

It is advisable to have the flask in a draft cupboard, as the hydrogen compounds of antimony and arsenic are very poisonous.—I am, &c.,

S. ERNEST LINDEN.

Oakfield, Buckhurst Hill, N.E.,
August 27, 1890.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Leeds Meeting of the British Association:—

President—Professor T. E. Thorpe, B.Sc., Ph.D., F.R.S., Treas.C.S.

Vice-Presidents—Professor P. Phillips Bedson, D.Sc., F.C.S.; Professor H. B. Dixon, M.A., F.R.S., F.C.S.; J. H. Gladstone, Ph.D., F.R.S.; Professor G. H. Liveing, M.A., F.R.S.; Dr. W. H. Perkin, F.R.S.; Sir H. E. Roscoe, D.C.L., F.R.S.; Dr. Schunck, F.R.S.; Professor A. Smithells, B.Sc., Ph.D., LL.D., F.R.S., F.C.S.

Secretaries—C. H. Bothamley, F.C.S., F.I.C.; H. Forster Morley, M.A., D.Sc., F.C.S. (*Recorder*); Dr. D. H. Nagel, M.A.; Dr. W. W. J. Nicol, M.A., F.R.S.E.

Committee—A. H. Allen; Professor H. E. Armstrong, F.R.S.; R. W. Atkinson; Dr. Vidor Auger; Dr. G. H. Bailey; Professor F. Clowes; George Duncan; Professor W. R. Dunstan; T. Fairley; A. E. Fletcher; Professor P. F. Frankland; Professor W. Noel Hartley, F.R.S.; A. G. V. Harcourt, F.R.S.; Professor Van't Hoff; Professor J. J. Hummel; B. P. Lascelles; Professor H. M'Leod, F.R.S.; Sydney Lupton; Dr. Stevenson Macadam; Professor R. Meldola, F.R.S.; M. M. P. Muir; Professor W. Ostwald; Dr. A. Pauli; Professor W. H. Perkin, F.R.S.; S. U. Pickering, F.R.S.; Professor W. Ramsay, F.R.S.; R. Reynolds; Dr. A. Richardson; Dr. S. Rideal; Dr. S. Rubemann; G. F. Schacht; W. A. Shenstone; Professor H. Lloyd Snape; W. Thomson; V. H. Veley; J. Ward; R. Warington, F.R.S.; Dr. J. Watts; J. J. Wertheimer; Professor A. W. Williamson, F.R.S.

The Papers brought before the Section were as follows:—

President's Address.

Report of the Committee on the History of Chemistry.

Report of the Committee on the Silent Discharge of Electricity in Gases.

Report of the Committee on the Present Methods of Teaching Chemistry.

Sir Henry Roscoe, F.R.S.—On Recent Legislation as Facilitating the Teaching of Science.

Dr. J. H. Gladstone, F.R.S., and G. Gladstone.—The Refraction and Dispersion of Fluorobenzene and allied compounds.

Dr. G. H. Bailey and J. C. Cain.—A method of Quantitative Analysis by Weighing Precipitates Suspended in Liquids.

Dr. G. H. Bailey and A. A. Read.—The Behaviour of the more stable Oxides at High Temperatures.

Dr. G. H. Bailey.—The spectra of the Haloid Salts of Didymium.

W. Hepworth Collins.—The Condition of the Air in Public Places of Amusement.

Report on Isomeric Naphthalene Derivatives.

Dr. W. H. Perkin, F.R.S.—The Development of the Coal Tar Colour Industry since 1880 (illustrated by specimens).

Professor J. H. Van't Hoff.—Behaviour of Copper Potassium Chloride and its Aqueous Solutions at different temperatures.

Report of the Committee on the Action of Light on the Hydracids of the Halogens in presence of Oxygen.

Professor Living, F.R.S., and Professor Dewar, F.R.S.—Experiments on the Combustion of Gases under Pressure.

Professor H. B. Dixon, F.R.S., and J. A. Harker.—The Rate of Explosion of Hydrogen and Chlorine in the dry and moist states.

Dr. G. S. Turpin.—On the Ignition of Explosive Gaseous Mixtures.

Jas. T. Brown.—The Orthophote.

Report of the Committee on an International Standard for the Analysis of Iron and Steel.

Report of the Committee on the Influence of Silicon on the Properties of Steel.

Report of the Committee on the Properties of Solutions.

Report of the Committee on the Bibliography of Solution.

Dr. O. Pettersson.—Recent Swedish Investigations on the Gases held in solution by the Sea-water of the Skagerack.

Joint Discussion with Section A on the Nature of Solution and its connection with Osmotic Pressure, opened by S. U. Pickering, F.R.S., in a paper on "The Present Position of the Hydrate Theory of Solution." Professors Van't Hoff and Ostwald took part in the discussion.

Dr. J. H. Gladstone.—The Molecular Refraction of Substances in Solution.

P. J. Hartog and J. A. Harker.—An Apparatus for the determination of the Freezing-points of Solutions.

C. H. Bothamley.—The Sulphur Waters of Yorkshire.

T. H. Easterfield, B.A., and J. Mitchell Wilson, M.D.—The River Aire—a study in River Pollution.

Report of the Committee on the Bibliography of Spectroscopy.

Report of the Committee for preparing a new series of Wave Length Tables of the Spectra of the Elements.

Report of the Committee on the Absorption Spectra of Pure Compounds.

Prof. T. E. Thorpe, F.R.S.—On Phosphorous Oxide.

Prof. R. Meldola, F.R.S.—Diazo-amido-compounds; a Study in Chemical Isomerism.

A. G. Green, C. F. Cross, and E. J. Bevan.—On the Action of Light on the Diazo-compounds of Primuline and of Dehydrothiolutidine; a Method of Photographic Dyeing and Printing.

Prof. J. J. Hummel.—Fast and Fugitive Coal-tar Colours.

T. Fairley.—Some Reactions of Hydrogen Peroxide.

Dr. Ahrens.—Veratrin, and the Existence of Two Isomeric β -picolines.

C. H. Bothamley.—Action of Phosphorus Trichloride on Organic Acids and on Water.

Prof. W. H. Perkin, Jun., F.R.S.—The Constitution of the Alkaloid Berberin.

J. E. Marsh and R. Stockdale.—The Production of Camphor from Turpentine.

T. Fairley.—A Continuous Aspirator.

W. Thomson.—Note on the Vulcanisation and Decay of Indiarubber.

W. Thomson.—On the Unburned Gases Contained in the Flue Gases from Gas Stoves and Other Burners.

Dr. J. Lewkowitsch.—Some Points on the Analysis of Fats.

Dr. T. Ewan.—Condensation of Dibenzyl Ketone with Oxalic Ether.

TO CORRESPONDENTS.

H. H.—Hofer's "Histoire de la Chimie." The work is in French, and we are not aware of an English version. Concerning the price, we must refer you to any foreign bookseller in London.

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H. W. HOLDER, M.A., Registrar.

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THE LONDON HOSPITAL MEDICAL COLLEGE.—THE WINTER SESSION will commence on Wednesday, October 1st.

The Hospital, which is the largest general hospital in the kingdom, contains nearly 800 beds, all in constant use. There are wards for accidents, surgical and medical cases, diseases of women and children, and ophthalmic cases. Special departments for diseases of the eye, ear, throat, skin and teeth, and for cancer, tumours, diseases of the bladder, piles and fistula. Number of in-patients last year, 9105; out-patients, 109,839; accidents, 11,400.

Surgical operations daily.
APPOINTMENTS.—Resident accoucheur, house physicians, house surgeons, &c. Forty of these appointments are made annually. Numerous dressers, clinical clerks, post-mortem clerks, and maternity assistants are appointed every three months. All appointments are free. Holders of resident appointments are also provided free board. Two Entrance Science Scholarships, value £75 and £50, and two Buxton Scholarships, value £30 and £20, will be offered for competition at the end of September to new Students. Sixteen other Scholarships and prizes are given annually.

The London Hospital is now in direct communication with all parts of the metropolis. The Metropolitan, District, and other railways have stations within a minute's walk of the Hospital and College.

For further information apply, personally or by letter, to—

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THE CHEMICAL NEWS.

VOL. LXII. No. 1608.

ADDRESS TO STUDENTS.

As the season comes round we are again led to call attention to certain points relating to higher education which, often as they have been raised, are still neglected. The claims of chemistry—and indeed of the physical and natural sciences altogether—to a much larger share of attention have been urged upon educators and students chiefly upon the ground of utility. This plea has been met with the sneering remark that we are not all going to become calico-printers, or iron-masters, tanners, or soap-boilers.

But we submit that physical and natural science—in a word, the study of *things* in contradistinction to *words* and *abstractions*—is entitled to eminence as an instrument of intellectual culture. Without it we can never, unless exceptionally gifted by nature, acquire the art of observation. In our present educational curricula, alike in board-school and grammar-school, this art is not merely left untaught, it is crowded out and starved at the very roots because the energies of the student are drawn off in other directions. A gentleman whose duty it became at one time to administer the somewhat homœopathic doses of science admitted at a public school puts on record the fact that the boys of the lower forms assimilated more readily than the seniors the elementary truths of chemistry and physics. The intellects of the latter had been so modified by a persistent course of verbalism that they could not see any meaning in *things*.

In like manner many working-men, possessing but a very scanty knowledge of the "three r's," were very good observers in botany, entomology, ornithology, &c. But the number of such men is certainly not on the increase. Indeed, an acute contemporary some years ago expressed the fear that the "vice of inobservance," so conspicuous among our upper classes, was being spread to the great mass of the nation in consequence of the exclusively literary character of our present system of education.

Yet, again, we may even venture to say that savages are often better observers than civilised Europeans or Americans, unless the latter have been systematically trained in research. More than one scientific traveller, on noticing some rare and curious plant, has been told by a "Redskin" in Texas or by a "Black fellow" in Queensland where such plant could be found in quantity.

Now the only way to escape from our present humiliating inferiority as observers is to give to natural and physical science a leading place in our courses of instruction. And as the mass of the public are now cooped up in towns the sciences to which their attention must mainly be directed are chemistry and physics.

But one caution must be kept in mind. The question how we are to learn is not less important than its companion what we are to learn. The youth who studies chemistry from books, however closely and laboriously, will reap little or no advantage from his labours. If he has done nothing further than read

he will still be in the bonds of verbalism, unable to learn from and to interpret phenomena.

It need scarcely be said that the main prop of verbalism is the examinational system. It is truly painful to have to remind our readers how completely the great protest against this system appears to have been forgotten, and how completely success in these displays is regarded as a triumph.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree granted by this University are required to have passed the Matriculation Examination, and all candidates for Matriculation will henceforth be required to comply with the following instructions:—(1) Not less than five weeks before the commencement of the Examination every candidate must apply to the Registrar, by letter, for a Form of Entry, which, together with all particulars respecting the arrangements for the Examination, will be sent to him immediately on receipt of the application. (2) This form, duly filled up, must be returned to the Registrar not less than four weeks before the commencement of the Examination, and with it, in the same cover, must be sent (a) the candidate's certificate of age, and (b) his fee for the Examination. No candidate's name will be placed on the list of candidates unless his form of entry, certificate of age, and fee shall have been received at the University on or before the fourth Monday before the commencement of the Examination. In the course of the week following the closing of the list, but not previously, each candidate's certificate and fee will be acknowledged, his certificate will be returned, and a Number, by which he is to be designated throughout the Examination, will be assigned to him.

The Fee for this examination is £2.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June. The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages:—Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Experimental Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds—their chief physical and chemical characters—their preparation—and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either

at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will be held in July, 1891.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original printed Dissertation or Thesis (at least six copies) treating scientifically some special department of the subject so named, embodying the result of independent research, or showing evidence of his own work, whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. The Dissertation or Thesis shall have been written in view of candidature, or shall have been

published within the two academical years immediately preceding. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published, and every contribution so specified and submitted shall be considered and taken as part of his qualification for the Degree. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, and with especial reference to his Dissertation or Thesis.

Candidates for the Degree of D.Sc. will be expected to be so fully conversant with the branch of Science they profess as to be able, if required, to satisfy any test of their acquirements in that branch that it may be thought expedient to apply.

The Fee for this Examination is £10.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination, nor unless he have given notice of his intention to the Registrar at least one calendar month before the commencement of the examination.

The Fee for this examination is Five Pounds.

EXAMINATION IN SUBJECTS RELATING TO PUBLIC HEALTH.

A Special Examination will be held in December in subjects relating to public health.

No candidate is admitted to this Examination unless he has passed the Second Examination for the Degree of Bachelor of Medicine in this University at least one year previously; nor unless he shall have given notice of his intention to the Registrar at least two calendar months before the commencement of the Examination.

The Fee for this Examination is £5.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; from the professors; and from the Sub-Librarian in the Radcliffe Library or the Museum.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass at the same time in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

examination in Classics and Mathematics, which may be done in the first or second term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £80 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, Downing, and Cavendish Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN. TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, M.D., F.R.S., V.P.C.S.

Assistant Lecturer.—Emil A. Werner, F.C.S., F.I.C.

Demonstrator.—William Early, F.I.C.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; advanced, second year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry.—J. M. Thomson, F.C.S.

Demonstrator of Practical Chemistry.—G. S. Johnson, F.C.S.

Assistant Demonstrator.—Herbert Jackson, F.C.S.

On Tuesday and Thursday at 10.20 a.m. Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction

are discussed, and the Non-metallic elements and their principal Compounds are described.

The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated.

Examinations of the Class, both *visd voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, on Tuesday and Friday, at 10.20, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis.

Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra Fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own Experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry—One Month (daily attendance), £4 4s. od.; Three Months (daily attendance), £10 10s. od.; Six Months (daily attendance), £18 18s. od.; Nine Months (daily attendance), £26 5s. od. A student taking a month's ticket may attend daily during 1 month, or 3 days a week during 2 months, or 2 days a week during 3 months.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1890-91, are Tuesday, September 30, Wednesday, January 14, and Wednesday, April 15.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is made to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery. The instruction given to each student is regulated by his special requirements.

PHOTOGRAPHY.

Lecturer.—J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third

year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professors.—R. T. Plimpton, Ph.D., and J. N. Collie, Ph.D.

The Session is divided into three Terms, as follows, all the dates being inclusive:—

First Term, from Thursday, October 2nd, until Friday, December 19th;

Second Term, from Tuesday, January 6th, 1891, till Wednesday, March 25th;

Third Term, for Lectures, from Tuesday, April 14th, till Wednesday, July 1st. Class Examinations occupy about ten days, beginning on Thursday, June 18th.

Students, who having entered in October do not intend to present themselves in all three subjects at the July Preliminary Science Examination, should during the first term confine their attention to Chemistry, and take this subject alone at the January Examination.

Students entering in January should take Physics and Biology at the July Examination, and Chemistry at the succeeding January Examination.

Junior or Matriculation Course.

Tuesday, Thursday, and Saturday, at 10, commencing October 7, 1890, and April 14th, 1891. Fee:—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms: Inorganic.—The Class meets four times a week: Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises, commencing October 6th.

Fee:—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Intermediate Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee:—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second

Term; and Monday, Wednesday, and Friday, at 9, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course for those engaged in prosecuting research in Organic Chemistry will be held three times a week during the Second Term. Fee, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11, commencing October 7th.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term.

Fee:—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London:—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite preliminary knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1890-91; also the Clothworker's Scholarship of £50.

Chemical Technology.

Lecturer, Watson Smith, F.I.C., F.C.S.

Courses of Lectures will be given on the following subjects:—Manufacture of Sulphuric Acid, Alkali, &c. Fuel and Gas Manufacture. Chemical Technology of Building Materials. Coal tar Products and Colours. Applications of Chemistry to Engineering.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

Residence for Students.

Students can obtain residence at University Hall, Gordon Square. Particulars can be obtained at the office of the College.

**NORMAL SCHOOL OF SCIENCE AND
ROYAL SCHOOL OF MINES.**

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.
Assistant Professor.—F. R. Japp, M.A., LL.D., F.R.S.
Demonstrators.—H. Chapman Jones and A. E. Tutton.
Assistants.—G. S. Newth, J. W. Rodger, and W. Tate.

The Normal School of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is affiliated to the Normal School. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Normal School. The instruction in the Normal School is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Normal School, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Normal School of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 1st of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidate being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Agriculture	4	10
Astronomical Physics	2	

Mathematics and Mechanical Drawing, £3 per term. Geometrical Drawing £3 per session. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Normal School of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Science teachers actually engaged in teaching who are registered by the Science and Art Department as qualified to earn payments for teaching Science may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Three courses of evening lectures for working men will be given during the session in Astronomy, Chemistry, and Mechanics. The admission to each course of six lectures will be 6d. The number of tickets is limited by the size of the lecture theatre.

**UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.**

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Göttingen), F.I.C.

Demonstrator.—A. W. Warrington, M.Sc. (Vic.), F.I.C.

The College is open to male and female students above the age of sixteen years. The Session commences on Monday, September 29, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly during the Lent and three during the Easter Term. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. For those Students who have selected Physics or Botany instead of Chemistry at the Matriculation Examination, an Introductory Course of three lectures weekly will be delivered during the Michaelmas Term. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term.

The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 17, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, George McGowan, Ph.D., F.R.S.E.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. Demonstrator, David M. Lewis, M.A.

The Session opens September 30th, 1890. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Elementary Physical Chemistry. Fee for the Term, £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Agricultural Chemistry.—Fee, £1 1s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s.

A Committee has been appointed to frame a complete scheme of Agricultural Instruction for North Wales, and the College has received a grant of £400 from the Board of Agriculture. Three Dairy Schools in connection with the College have been established in Welshpool, Denbigh, and Bangor, and an Agricultural Department will be opened next session, in which students may receive a complete training in Agricultural Science.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—G. S. Turpin, M.A., D.Sc.

The Session commences October 6th, and terminates in June, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 90 lectures in continuation of the Junior Course, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee £3 3s.

The Senior Course includes some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

An Elementary Organic Course of 10 lectures, and a course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Professors Thompson and Parker are recognised by the Universities of Edinburgh, Glasgow, and Aberdeen as teachers in Chemistry and Natural History respectively, so that registered Medical Students can spend one year of their course at the University College, Cardiff. The College is also recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Female Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc.

Lecturer.—Arthur Richardson, Ph.D.

The session 1890-91 will begin on October 1st. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articulated pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is affiliated to the College. Several Scholarships are tenable at the College. Full information may be obtained of the Secretary.

DAY LECTURES.

Inorganic Chemistry.

The Course treats of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Lectures will be given daily at 10 and 11 o'clock.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it is closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures, and to Scouring, Bleaching, and Dyeing. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session ..	15	13	10	7½	5
„ Two Terms ..	11	9	7½	5½	4
„ One Term ..	6	5	4	3	2
„ Month ..	3	2½	2	1½	—

Students may arrange to divide their days of laboratory work into half-days.

Analytical Course.

A Course of Lectures on the Principles of Qualitative Analysis will be given during the First and Second Terms; it is intended to supplement the instruction in Practical Chemistry. All first year's Laboratory Students are expected to attend this Course. The Lectures will be given on Mondays at 10 a.m. Fee, £1 1s. for the two Terms.

Photographic Chemistry.

Instruction will be given in the Photographio Laboratory in Dry-plate Processes, Printing, Enlarging, and in Microscopical Photography, at times to be arranged with those who enter. Fee, £3 3s. for each Term.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures.

A course of Lectures will also be delivered on Photographic Chemistry. Fee for each course, 7s. 6d.

With the approval of the Council of the Institute of Chemistry students desiring to qualify as Associates may pass through the requisite amount of study at this College, which has also been approved as a centre for the Practical Examination of the Institute.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc. Lond., F.R.S.

Assistant Lecturers.—W. W. J. Nicol, M.A., D.Sc. Edin., and Thomas Turner, Assoc.R.S.M., F.C.S.

Demonstrator.—T. Rhymer Marshall, D.Sc. Edin.

The Session will be opened on Tuesday, September 30th 1890.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for B.Sc. and Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also

satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays, at 9.30 a.m. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday and Wednesday at 9.30 a.m. Fee, £1 11s. 6d.

Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once or twice a week. Fee for the session, £3 3s.

Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Three Terms	18 „	12 „

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course. A more advanced course upon selected subjects is also given by Mr. Turner, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Professor.—Christopher Rawson, F.I.C., F.C.S.

Demonstrator.—Percy Kay.

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The

Session began on September 15th and terminates on July 10th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—A. G. Bloxam, F.C.S., A.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.C.S.

Assistant Lecturers.—C. H. Bothamley, F.C.S., and Herbert Ingle, F.C.S.

The Session begins October 7, 1890.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First years' Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Inorganic Chemistry.—Second years' Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday and Thursday at 11.30 p.m. Fee £2 12s. 6d.

5. Theoretical Chemistry.—Advanced Course. Fee, £1 11s. 6d.

6. Chemistry as Applied to Coal Mining.—Tuesday during the First Term, at 4 p.m.

7. Photographic Manipulation.—A Course of Ten Lessons will be given on Fridays, from 2 to 5, during the Third Term, with special reference to dry plate processes and silver and platinum printing. Fee, £1.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—On Tuesday and Thursday, from 10 to 12 a.m., from May to July.

Evening Classes.

A Course of twenty Lectures by Mr. C. H. Bothamley, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 9. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.C.S.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the new 1851 Exhibition Scholarships.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Demonstrators.—C. A. Kohn, B.Sc., Ph.D., and T. L. Bailey, Ph.D.

Assistant.—H. H. Frousell.

The Session commences October 2nd.

The Classes are arranged to suit the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry.

Course A.—Non-metals.

Course B.—Metals.

Course C.—Organic Chemistry.

Course D.—Physical Chemistry.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy.

Course F.—Technological Chemistry: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Distillation of Coal, and Tar Industries. (4) Fuel. (5) Chemistry Applied to Sanitation. (6) Technical Gas Analysis. (7) Spectroscopy.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Special: For the Conjoint Board of Colleges of Physicians and Surgeons. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class: Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Inter-mediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

TABLE OF FEES.

Per Week.	One Month.	One Term. Three Months.	Two Terms. Six Months.	Three Terms. One Session.
One day ..	—	£4	£6	£8
Two days ..	—	6	8	10
Three days..	£4	8	10	12
Four days ..	5	9	12	15
Five days ..	—	10	14	18

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

Technological Curriculum.

First Year.—Chemistry, either the Elementary Course or Course A, according to the previous knowledge of the Student. Practical Classes 1 and 2. Mathematics and Mechanics. Engineering Drawing and Design (in this or the following year). French or German. Physics.

Second Year.—Chemistry—Courses A and B; Chemical Laboratory three days per week, and the Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work. Mathematics (intermediate). German. Intermediate B.Sc. Examination may be passed.

Third Year.—Chemistry, Lecture Course on Organic Chemistry, C, Lecture Course E, Technological Chemistry, Course F. Chemical Laboratory. Engineering, Mathematics, or Physics (advanced). The Final Examination for the Victoria B.Sc. may be taken, or the Examination for the associateship of the Institute of Chemistry.

Fourth Year.—Courses D and F; part of Course C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

Evening Classes.

Lectures will be given on the Chemistry of Photography, and Copper and its Manufacture.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, and a Sheridan Muspratt Exhibition of £25 per one year, will be awarded in December, 1891, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Prospectus containing full particulars may be obtained from F. and E. Gibbons, 19, Ranelagh Street, Liverpool, price 6d.; or from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

**DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-ON-TYNE.**

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Assistant Lecturer and Demonstrator.—Saville Shaw, F.C.S.

The Session will commence on September 29th, 1890.

Junior Division: First Year Course.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 8th.

Senior Division: Second Year Course.—A Course of about ninety Lectures will be given throughout the Session the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and will commence on Tuesday, October 9th.

Fee, for either Course, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for each course, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 13th. Fee, £1 1s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. **Laboratory Fees.**—Students working six days per week, £5 5s. per term; alternate days, £3 3s.; one day per week, £1 1s.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.
2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in three, at least, of the five subjects,—Mathematics, Physics, Chemistry, Geology, and Biology,—in an examination, to be held at the beginning of his second year.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 29th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE,
VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—C. Schorlemmer, LL.D., F.R.S.

Demonstrators and Assistant Lecturers.—Julius B. Cohen, Ph.D., and George H. Bailey, D.Sc., Ph.D.

Assistant Demonstrators.—A. Harden, Ph.D., and G. Fowler, B.Sc.

Lecturer in Dyeing and Printing.—Ernest Bentz.

The Session begins on October 7, 1890, and ends on June 26, 1891.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 10.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honour Course.—Mondays, Wednesdays, and Fridays, 3.30 p.m., during the two Winter Terms. The Non-Metals.

Second Year Honour Course.—Mondays, Wednesdays, Fridays, 9.30, during the two Winter Terms. The Metals.

Third Year Honour Course.—Tuesdays, 11.30. Physical Chemistry.

Organic Chemistry (Honours).—Tuesdays, Thursdays, Saturdays, 9.30, during the Session.

History of Chemistry and Chemical Philosophy.—Thursdays, 10.30, during the Session.

An ordinary degree of B.Sc. in Chemistry, Victoria University, may be taken at the College in either two or three years, according as the student passes the Preliminary Examination on joining the College or whether he takes a year to prepare for that examination. The Degree of B.Sc. with Honours in Chemistry can be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Exhibitions, &c., are available to students.

Technological Chemistry.

First Course.—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of Coal Tar.

Fourth Course.—Natural and Artificial Dye-stuffs.

Fifth Course.—Calico-printing.

Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Honours Course on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third

years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physics laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENT OF CHEMISTRY.

Professor of Chemistry.—Frank Clowes, D.Sc. Lond., F.I.C., F.C.S.

Demonstrators.—J. B. Coleman, A.R.C.Sc. Dublin, F.I.C., F.C.S., and R. L. Whiteley, F.I.C., F.C.S.

Lecturers.—J. B. Coleman, F.I.C., F.C.S.; R. L. Whiteley, F.I.C., F.C.S.; C. Haydon White, M.R.C.S.; J. W. Carr, M.A.; and F. R. Sargeant.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1890-91 will be as follows:—First Term, October 6th to December 20th; Second Term, January 19th to April 4th; Third Term, April 20th to July 4th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry in the third term. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes, 50s. for the session of three terms: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day except Saturday from 10 to 5, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees.—For one term, £6; for the session, £15; for day students for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

Courses of Technical Chemistry Lectures are also given on Dyeing and Bleaching, Brewing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

A *Pharmaceutical Curriculum* extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), and Practical Dispensing,

taught by demonstrations and practical work in the laboratory.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonstrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 2s. 6d.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc., F.C.S.

Demonstrator and Assistant Lecturer.—L. T. O'Shea, B.Sc., F.C.S.

The Session will commence on Friday, October 3.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Thursday, from 10 to 11 a.m. Fee, £3 3s.

Second Year's Course.—Chemistry of Metals. Tuesday, Wednesday, and Thursday, from 10 to 11 a.m. £3 3s.; or for the First and Second Courses, £5 5s.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.; Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for six or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Monday and Wednesday, 6 to 9. Sessional Fee, one evening per week, £1 10s.; two, £3; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

(UNIVERSITY OF ST. ANDREWS).

Professor.—Percy F. Frankland, Ph.D., B.Sc., F.I.C., &c.

Assistant Lecturers and Demonstrators.—F. J. Hambly, F.C.S., and J. R. Appleyard, F.C.S.

The eighth session of the College will be opened on October 14th, 1890.

The Lectures and Laboratory practice in this University are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the Universities of Edinburgh, Glasgow, and Aberdeen.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as at-

tendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: Inorganic Chemistry (Non-Metals) (90 lectures), Monday, Wednesday, and Friday, from 10 to 11 a.m.; fee, £3 3s.

Second year's lecture course: 1. Inorganic Chemistry (Metals) (40 lectures), Tuesday and Thursday, from 9 to 10 a.m.; fee, £1 11s. 6d. 2. Organic Chemistry (50 lectures), Tuesday, Wednesday, and Thursday; fee, £1 11s. 6d.; fee for the entire year's course, £3 3s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory and Dyehouse. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also arranged for students preparing for their medical and pharmaceutical examinations. A three months' course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 3 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction.

Forster Research Scholarship.

This scholarship, of the value of £30, is awarded annually to the best student on the condition that he devotes himself during the ensuing year to original research in the College Laboratory.

UNIVERSITY OF EDINBURGH.

Professor.—A. Crum Brown, F.R.S.E.

Two degrees in Science are conferred by the University of Edinburgh, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.). Both these degrees are conferred in Physical and Natural Science, in Public Health, and in Engineering.

Candidates for degrees in Physical and Natural Science

must pass a preliminary examination in English, Latin, Arithmetic, the Elements of Mathematics, and the Elements of Mechanics, and in at least two of the following subjects:—Greek, French, German, Higher Mathematics, Natural Philosophy, Logic, and Moral Philosophy.

The First B.Sc. Examination embraces Mathematics, Natural Philosophy, Chemistry, Zoology, including Comparative Anatomy, and Botany. The Second B.Sc. Examination the Higher Mathematics, Experimental Physics, Chemistry, Zoology, Botany, Physiology, and Geology, including Palæontology and Mineralogy.

The D.Sc. Examination embraces Mathematics, Natural Philosophy, Applied Mathematics, Experimental Physics, Practical Astronomy, Chemistry, Zoology and Comparative Anatomy, Animal Physiology, Botany, and Geology, including Palæontology and Mineralogy.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Copies of the Calendar for 1890-91 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry.—T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 29th. A Competitive Examination, open to intending Students of Arts or Science, for a number of Entrance Bursaries, ranging in value from £30 to £10 each per annum, will be held during the last week of October. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), the regulations regarding which will be found in the "University Calendar."

Lecture Course.

A Lecture is delivered by the Professor of Chemistry, at 11 o'clock, on five days in the week throughout the Winter Session. The Course commences with the study of a few typical substances, forming an introduction to the discussion of Chemical Theory; the Non-metallic and Metallic Elements, with their chief compounds, are then considered; and the latter part of the Course is devoted to Elementary Organic Chemistry. Three Lectures weekly are of an elementary character, and are intended to be useful to Students of Arts who desire to study Chemistry as a branch of general education, or with the view of teaching it in schools; the remaining two Lectures weekly constitute a Supplementary Course, framed so as to meet the additional requirements of Candidates for the Degree of Bachelor of Science and of Medical Students.

Certificates are awarded on the results of separate examinations on the subjects of the general and supple-

mentary Lectures, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, £3 3s.

Laboratory Course.

A class in Practical Chemistry meets for two hours weekly, to which Students attending the Lectures are admitted without additional fee. The Course consists of a series of qualitative and quantitative experiments, designed to give the Student a practical acquaintance with the principles of Chemistry regarded as a subject of general education.

The Laboratory is also open during the Session from 10 a.m. to 4 p.m., for instruction in Chemical Analysis. The fee is £10 10s. for the Session. Shorter Courses of Practical Chemistry will be arranged to meet the requirements of Students who cannot give so much time to the subject, the fees for which vary according to the number of hours taken weekly.

Several free places in the Laboratory will be given to Students desirous of engaging in original work. Applicants must satisfy the Professor that their studies are sufficiently advanced to admit of them prosecuting experimental research.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on two days of each week after May 1st. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given from the beginning of the Session, on Tuesdays and Thursdays, at 10 a.m., until the beginning of April, and at 3 p.m. after May 1st.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the beginning of April, and from May 1st until the middle of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

QUEEN'S COLLEGE, CORK.

Professor.—Maxwell Simpson, LL.D., M.D. (Hon.), F.R.S., &c.

The Course of Theoretical Chemistry is divided into Inorganic and Organic Chemistry.

In the first part are discussed the Laws of Combination and Affinity, Molecular Chemistry, and the History of the Non-Metallic and Metallic substances.

In the Organic portion of the Course will be considered the subjects of Organic Analysis, Organic Series, Compound Radicals and Types, Metamorphosis of Organic Bodies, History of Special Animal and Vegetable Bodies.

In treating of the Laws of Chemistry, and the History of Inorganic and Organic Bodies those points will be chiefly dwelt upon which have a practical bearing in the Arts, Medicine, Engineering, and Agriculture. Hence, during the Course, attention will be directed to the application of Chemistry to Medicine and Physiology, to Metallurgic Operations, Chemical Manufactures, Building Materials, Soils, and Manures.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

The Chemical Laboratory is open daily except on Saturdays, from 10 to 4 o'clock, under the Superintendence of the Professor, to Students desirous of prosecuting an extended course of qualitative and quantitative analysis, and for the purpose of original investigation in connection with the Arts, or in the higher departments of Scientific Chemistry.

The Course of Practical Chemistry consists of about thirty-nine Lectures, and will commence at the beginning of the Second Term. Fee for each Sessional Course £3.

**ROYAL COLLEGE OF SCIENCE FOR IRELAND,
STEPHEN'S GREEN, DUBLIN.**

(SCIENCE AND ART DEPARTMENT).

Professor of Practical and Theoretical Chemistry.—W. N. Hartley, F.R.S.

Assistant Chemist.—T. A. Shegog, F.C.S., A.R.C.S.

The Session commences on Monday, October 6, 1890.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures. The Diploma in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry, (2) Applied Chemistry, (3) Analytical Chemistry, (4) Instructions in Chemical Research.

Fees payable by Associate Students in the Faculty of Manufactures:—For the entire Course—first year, £13; second year, £23; third year, £14.

Fees payable by Non-Associates:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months; £12 for the entire session.

The following are supplementary courses of instruction for beginners:—

Laboratory Instruction in the Theory of Chemistry, February, March, April, and May, Tuesdays and Thursdays, 10 a.m. till 1 p.m. Fee for the Course, £4.

A Course of Lectures on Elementary Chemistry by the Assistant Chemist, February, March, April, and May, Wednesday, 3 to 4 o'clock. Fee for the Course, 10s.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are given to Associate Students, not being Royal Exhibitors, who have been a year in the College on the results of their examinations. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Science Examinations of the Department of Science and Art.

**CHEMICAL LECTURES, CLASSES, AND
LABORATORY INSTRUCTION.**

**CITY AND GUILDS OF LONDON INSTITUTE FOR THE
ADVANCEMENT OF TECHNICAL EDUCATION.**—*Central Institution, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given in this Institution is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing

offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged.

Technical College, Finsbury.—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments:—1. Mechanical Engineering; 2. Electrical Engineering and Instrument-making; 3. Manufacturing Chemistry, and Industries involving the application of Chemistry; 4. The Art Industries, including Cabinet-making and Decoration in Colour and in Relief; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 30th, 1890, and the work of the Session will commence on October 7th.

**BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION,
BREAM'S BUILDINGS, CHANCERY LANE.**—*Chemistry:* Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry:* Mr. G. Chaloner, F.C.S. Lectures—Elementary, Tuesdays, 8.30 p.m.; Advanced, Thursdays, 7 p.m.; Practical, Tuesdays, 6–8 p.m.; Thursdays, 8–10 p.m.; Saturdays, 7–9 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 7.30 p.m.; Advanced, Wednesdays, 8.45 p.m.; Practical, Wednesdays, 6–7.30 p.m.; Fridays, 6–10 p.m.

**SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT
BRITAIN,** 17, Bloomsbury Square, London, W.C.—Professor of Chemistry, Wyndham R. Dunstan, M.A., F.C.S. Professor of Practical Chemistry, John Attfield, Ph.D., F.R.S. In this school, which is specially intended for Pharmaceutical Students, Courses of Instruction are given in the sciences of Chemistry (Physical, Inorganic, and Organic) and Botany, as well as in their applications to Pharmacy and Medicine. Professor Dunstan delivers during the Session (October to July) two Courses of Lectures on Chemistry; an Elementary Course from October to March and an Advanced Course from April to July. The Laboratories for practical instruction in Chemistry under the direction of Professor Attfield are open daily throughout the Session. Particulars respecting Scholarships, Medals, and Prizes, as well as other information relating to the School, may be obtained on application.

CHARTERHOUSE SCIENCE AND ART SCHOOLS.—The Winter Session commenced on Tuesday, September 16th, 1890, under the presidency of the Rev. H. Swann, M.A. Classes are established in this institution by which instruction of a practical character is given in most of the Sciences at a very nominal fee; whilst in Art, at an equally low rate, Students, under the direction of five competent instructors, can be advanced in their studies. Those who have leisure can, at a very moderate charge, attend the Day Classes in

Art. Day Classes will also be held to prepare Candidates for Matriculation (Lond.), the Clerical, Medical (including Dental), Legal, and other Examinations. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working in a well-fitted Laboratory, capable of accommodating sixty Students. Aspirants for University Honours can at a small expense be assisted in their studies.

MIDDLESEX COLLEGE OF CHEMISTRY AND PHARMACY, 40, Charlotte Street, Portman Square.—Principal, F. H. Painter. Day and Evening Classes and Laboratory Instruction in Chemistry, Pharmacy, Materia Medica, &c.

THE CITY SCHOOL OF CHEMISTRY AND PHARMACY, 27, Chancery Lane, London, W.C.—Principal, Mr. Maurice Williams. Theoretical and Practical Chemistry, Chemical Physics, Theoretical and Practical Pharmacy, Materia Medica, and Therapeutics.

NEW CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S. Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

SOUTH LONDON SCHOOL OF PHARMACY, 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £10 10s. (junior) and £12 12s. (senior); afterwards £2 2s. and £3 3s. per month respectively, inclusive of all departments.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Chemistry, Mr. D. S. Macnair, Ph.D., F.C.S., assisted by Mr. G. Pope. The session commences Monday, September 29th. The classes are open to both sexes without limit of age.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on Monday, September 29th, 1890.

MORLEY MEMORIAL COLLEGE, ROYAL VICTORIA HALL, Waterloo Bridge Road, S.E.—Science and Technical Classes, Session 1880-91. Lectures will be given in the following subjects:—Principles of Chemistry, Electricity and Magnetism, Heat, Light, and Sound, and Mechanics. The instruction given is suited to artisans and practical men, and is chiefly in connection with the Science and Art Department, South Kensington. Classes begin Wednesday, October, 1st.

UNIVERSITY CORRESPONDENCE COLLEGE, 124, Booksellers Row, W.C.—The classes held at the Chemical and Biological Laboratories of University Tutorial College during the last Session were a marked success; no less than 27 students being successful at the Intermediate Science and Preliminary Scientific Examinations, of London University. The next Session commences the first week in October.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E.—Messrs. Wills and Wootton.

BRISTOL MEDICAL SCHOOL.—Mr. T. Coomber, F.C.S.

MERCHANT VENTURERS' SCHOOL, BRISTOL.—Head Master, J. Wertheimer, B.Sc., B.A. The Chemical and Metallurgical Laboratories are open to students of either

sex every week-day except Saturday, and students may either devote the whole of their time to laboratory work, or they may take the complete course of chemical training. Prospectus containing full particulars can be obtained at the School, or at the Merchants' Hall, price 4d.

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackney Hey, Liverpool.—Principal, Mr. A. Norman Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufacturing and plant, and construction of apparatus.

LEEDS SCHOOL OF MEDICINE.—Prof. Smithells.

MANCHESTER TECHNICAL SCHOOL.—Lecturers: Dr. E. Knecht, F.I.C., E. L. Rhead, J. Grant, F.C.S., and E. Milnes. The day classes commenced on Sept. 2nd, 1890, and the evening classes will commence on Sept. 22nd. The school is equipped with two large laboratories for the practical study of Pure Chemistry and Physics, a Laboratory for Metallurgy, and one for Dyeing, Bleaching, and Printing. Special practical work in any branch of Chemical Technology, or in preparation for University Examinations, will be arranged to suit individual Students. The Evening Courses of instruction are especially designed to meet the wants of those already engaged in various industries. A syllabus, containing full particulars as to hours, fees, &c., may be obtained from Mr. J. H. Reynolds, The Technical School, Manchester.

NEWCASTLE-ON-TYNE SCHOOL OF SCIENCE AND ART AND TECHNICAL COLLEGE (Chemical Department).—Principal, P. Hawkrigge, M.A., B.Sc. Lecturers and Demonstrators, W. D. Oliver, H. Oliver, J. D. Best, W. Carr, &c.

INSTITUTE OF SCIENCE AND ART, VALPY STREET, READING.—Head Science Master: Alfred J. Shilton, F.C.S. Session begins September 29th.

SHEFFIELD BOROUGH ANALYSTS' LABORATORY, 1, Surrey Street.—Mr. A. H. Allen, F.C.S. Day and Evening Classes.

STOCKPORT TECHNICAL SCHOOL.—Chemistry and Dyeing Department.—Lecturers on Chemistry: R. J. Brown, M.Sc., and G. W. Davies, F.C.S. Lecturer on Metallurgy: G. W. Davies, F.C.S. Lecturer on Dyeing: W. M. Gardner, F.C.S. There is a Chemical Laboratory to accommodate 120 Students, and also a Metallurgical Laboratory and a Dyehouse. There will be Day and Evening Courses of Lectures on Inorganic and Organic Chemistry and on Dyeing, Bleaching, and Calico Printing, and also practical instruction in the same, and in the evening there will be, in addition, Classes in Practical and Theoretical Metallurgy. In the Evening Classes the instruction is based mainly on the lines laid down by the Department of Science and Art, but in the Day Classes a more extended Course of instruction is pursued, and opportunity is afforded for carrying on any special branch of practical work under the supervision of the teachers. A Syllabus containing full particulars of times, fees, and courses of instruction is obtainable on application.

TECHNICAL INSTITUTE, SWANSEA.—Classes in Theoretical and Practical Inorganic and Organic Chemistry will be held during the winter months, commencing Oct. 4th, 1890. Principal, W. Morgan, Ph.D., F.C.S., F.I.C.

EDINBURGH SCHOOL OF MEDICINE, 41, Chambers St.—Dr. Drinkwater, F.C.S.—The instruction here qualifies for all Medical Boards, Edinburgh University, London University, &c. Day and Evening Classes.

SCHOOL OF MEDICINE, SURGEON'S HALL, EDINBURGH.—Dr. Stevenson Macadam, F.R.S.E., Mr. Falconer King, Mr. Ivison Macadam, Mr. Drinkwater, and Mr. Rymer.

SCHOOL OF MEDICINE, EDINBURGH.—The Laboratory, India Buildings, Edinburgh, is open throughout the year for Students, under the superintendence of J. B. Readman, D.Sc. F.R.S.E., F.C.S. Attendance at this laboratory qualifies for the Degrees of Medicine, Science, and Public Health of Edinburgh University, and for the Examinations in Medicine and Public Health of the Royal Colleges of Physicians and Surgeons, Edinburgh. Hours, 10 a.m. to 4 p.m.

SCHOOL OF MEDICINE, MINTO HOUSE (NEW VETERINARY COLLEGE, EDINBURGH).—Mr. J. Falconer King, F.C.S., F.I.C., and Mr. John Hunter, F.I.C., F.C.S.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

CHEMICAL LABORATORIES AND CLASS ROOMS.—Messrs. R. R. Tatlock and Readman, City Analyst's Laboratory, 156, Bath Street, Glasgow; and India Buildings, Edinburgh. The Laboratory is open daily all the year for the reception of students, under the immediate supervision of R. R. Tatlock, F.R.S.E., F.C.S., F.I.C., the City Analyst and Gas Examiner. Hours, 10 a.m. to 4 p.m.

GLASGOW VETERINARY COLLEGE.—Professor Cooke.

STIRLING SCHOOL OF SCIENCE AND ART.—Chemical and Physical Laboratories.—Andrew Wilson, F.I.C., and Assistants. Laboratory work daily, from 10 to 1. Lectures, 2 to 4 p.m.

QUEEN'S COLLEGE, GALWAY.—Dr. Dixon.

ROYAL COLLEGE OF SURGEONS IN IRELAND, DUBLIN.—Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

DUBLIN, CARMICHAEL COLLEGE OF MEDICINE.—Professor of Chemistry: C. R. C. Tichborne, Ph.D., F.C.S.

DUBLIN, CATHOLIC UNIVERSITY.—Dr. Campbell.

THE DETECTION OF TRACES OF IODINE IN THE PRESENCE OF MUCH CHLORINE.

By ALEXANDER JOHNSTONE, F.G.S.,
Assistant to the Professor of Geology and Mineralogy, Edinburgh University.

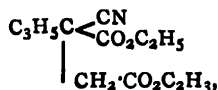
HAVING experienced considerable difficulty in rapidly determining by the usual tests the presence of iodine in the company of chlorides, in the course of some recent investigations on the properties of the naturally occurring halogen salts, I was led to devise the following simple method, by the use of which I believe I have been able to prove the wider occurrence of iodine in the mineral kingdom than has hitherto been supposed. To the properly prepared solution of the substance to be tested add a single drop of a saturated solution of silver nitrate in strong pure ammonium hydrate. If iodine is present even in the minutest quantity, the characteristic pale yellow precipitate of silver iodide will instantly form. Confirm this indication by pouring in—after having mixed the precipitate through the liquid by inverting the test-tube with the thumb on the orifice—pure concentrated sulphuric acid, which first deepens the yellow of the precipitate, and then, when sufficient has been added, liberates the iodine, which is readily and infallibly recognised by its unique appearances, whether precipitated to the bottom of the tube, suspended in the liquid, or dissolved through it to form a pink solution. If not a trace of iodine is present in the chloride tested, the latter will give no precipitate, or at most only a faint whitish cloud that will immediately disappear on the first shake given to the tube in the subsequent mixing.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

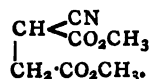
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 7, August 18, 1890.

New Synthesis effected by means of Cyano-succinic Ether. Acetylcyanosuccinic Ether.—L. Barthe.—The author has obtained this compound,—

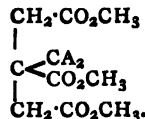


as a colourless oil.

Methyl Cyanosuccinate and Cyanotricarballylate. L. Barthe.—The former of these compounds has the formula—



The latter is—



Researches on Butter and Margarine.—C. Viollette.—The author distils in a confined atmosphere and in a current of watery vapour the fatty acids derived from about 50 grms. pure dry butter saponified with an aqueous solution of potassa. He collects not less than 10 litres of the condensation liquid obtained by allowing 17,000 litres of steam to bubble into the fatty acids suspended in water at 100°. An alkalimetric operation (using phenolphthalein as indicator) renders it possible to deduce the proportions of the butyric and caproic acids of the butter. The concrete volatile acids are weighed, as well as the fixed acids, after washing, desiccation in a vacuum, and fusion. The quantity of each of these groups renders it practicable to determine their equivalent, and, consequently, by calculating the glycerides, to effect the synthesis of the butter.

Researches on the Optical Analysis of Butters.—C. Viollette.—Butters and margarines have different indices of refraction, which show deviations of -33° to -27° of the oleorefractometer for butters, and of -15° to -8° for margarine. The indications of the oleorefractometer are sufficiently precise when they refer to mixtures the components of which have known deviations. It is necessary to fix, by a series of observations on different butters, the minimum deviation below which a butter may be considered as a margarine. The oleorefractometer may be useful for examining the butters of commerce, but its indications can be considered certain only when the butters show a deviation less than the lowest limit of butters.

On a Characteristic Reaction of Cocaine.—Ferreira da Silva.—The author treats a small portion of cocaine or of one of its salts in the solid state, or the residue from the evaporation of any of its solutions, with some drops of fuming nitric acid of sp. gr. 1.4. It is evaporated to dryness on the water-bath; the residue is treated with one or two drops of a strong alcoholic solution of potassa. On stirring up with a glass rod there is observed a special or distinct odour recalling that of peppermint.

No. 8, August 25, 1890.

Transformation of Melted Ammonium Nitrate.—E. Matthieu-Plessy.—According to the author, in preparing oxamic acid and oxamide by means of melted ammo-

nium nitrate there is formed a third product, the nitrate of a new fixed alkali. This fixed alkali is a substituted ammonia—a nitric monamide or nitramide. It may be named azotylamine; and its nitrate, azotylammonium nitrate.

MISCELLANEOUS.

The Chemical Laboratory of Wiesbaden.—In the Summer Term, 1890, there were 69 students on the books. Of these 42 were from Germany, 5 from Russia, 5 from North America, 4 from England, 4 from Austro-Hungary, 2 from France, 2 from Italy, 2 from Spain, 1 from Norway, 1 from Chili, 1 from South Australia. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged as teachers in the establishment Prof. Dr. H. Fresenius, Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. Med. G. Frank, and Architect J. Brahm. The assistants in the instruction laboratory are two in number, in the private laboratory seventeen, in the Versuchsstation three. The next Winter Term begins on the 15th of October. Besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and in the Versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Paper Manufacture.—(Reply to Richmond Villas).—As authorities on the paper manufacture in all its branches, we can recommend "The Art of Paper Making," by Alex. Watt (London: Crosby Lockwood and Son); also "Spon's Encyclopedia of Industrial Arts, &c.," Division IV. (Spon, Charing Cross). Appended to the latter is a fairly complete bibliography of the subject. In the same work, Division V., is an account of the starch manufacture.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1609.

ON THE DETERMINATION OF OXYGEN IN THE AIR.

By J. ALFRED WANKLYN and W. J. COOPER.

FOR the last half-century the methods for the determination of oxygen in the air have been explosion with excess of hydrogen, and absorption by means of pyrogallate of potash.

There is an old method founded on the wonderful reaction between nitric oxide and oxygen, which flourished soon after the discovery of the composition of the atmosphere, and was abandoned and is now almost forgotten, and never mentioned without being condemned.

We have had to investigate this process in the course of work undertaken in order to write our just published book entitled "Air Analysis." We find that when this old process—the process of Priestley and Cavendish—is altered in a very simple and obvious manner, it is rendered accurate, and we now present it to chemists as one of the most satisfactory processes in the whole range of analytical chemistry.

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The experimental details are given in our book.

ON THE DETERMINATION OF PHOSPHORIC ACID IN BASIC SLAGS.

By G. ARTH.

VARIOUS authors recommend precipitation by ammonium molybdate in order to determine the phosphoric acid in these slags, but without placing themselves in identical conditions. Some add the molybdic solution directly to the hydrochloric liquid obtained on attacking the slag and without removing the silica which may be in solution; others eliminate the silica, but still operate in presence of hydrochloric acid.

It is already well known that to separate phosphoric acid in the state of ammonium phospho-molybdate with accuracy the silica and the hydrochloric acid must be got rid of by transforming the bases into nitrates. Müntz evaporates the solution to dryness two or three times with nitric acid until the chlorine is expelled, and then adds the ammonium nitro-molybdate to the nitric solution.

Having had occasion to analyse one of these slags, the author treated it with hydrochloric acid, rendering the silica insoluble, and removing it in the usual manner, and he then evaporated the filtrate with nitric acid to expel chlorine. The following result was observed on operating thus with a sample containing 13.85 p.c. phosphoric acid. When the hydrochloric acid is about to disappear, generally during the second evaporation with nitric acid, there forms in the concentrated liquid a yellow, granular precipitate, which increases more and more and which cannot be re-dissolved in nitric acid, cold or hot, dilute or concentrated. As this precipitate contains phosphoric acid it is impossible to have here a nitric solution containing all the phosphorus.

The composition of the yellow deposit is that of a

hydrated ferric phosphate, $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$, after drying at 100° — 105° . It is soluble in strong hydrochloric acid, especially with the aid of heat.

This phosphate has the same composition as the ordinary precipitated phosphate, but the latter is nearly white and dissolves readily in the mineral acids even if diluted, whilst the other is far less soluble, and has a decided yellow colour. The two phosphates in question appear to be allotropic modifications of one and the same compound, presenting differences analogous to those noticed in ferric oxide itself, *e.g.*, as regards solubility. In fact, if they are treated with a cold potassa-lye they dissolve with different degrees of readiness, and yield two oxides, the appearance of which is decidedly different, while the filtrate contains the same phosphoric acid.

This new ferric phosphate is easily prepared from pure ferric chloride and disodic phosphate, evaporating the solutions with a sufficient excess of nitric acid.

In analytical operations this compound may be formed if the ferric oxide and the phosphoric acid in the substance are in a certain proportion, as it may be the case in basic slags.

By evaporating a mixture of ferric chloride, of disodic phosphate, and nitric acid, there is sometimes formed another tetrahydrated ferric phosphate of a rosy white colour, insoluble in nitric acid. This compound may be the one which Erlenmeyer obtained under different conditions.—*Annalen der Chemie und Pharmacie*.

DISINFECTION BY BURNING SULPHUR.*

By E. R. SQUIBB, M.D.

UNDER the head of Prevention Dr. Segur asks what are the important measures of prevention, and among these may certainly be included the disinfection of infected apartments.

Perhaps the most common measure for the disinfection of apartments which have been infected by diphtheria and other contagious diseases, is the burning of sulphur. This mode of disinfection has been in active use for more than a hundred years and many epidemics of contagion are supposed to have been controlled by it. Of late years, however, its efficacy and utility have been called in question by several prominent authorities on the ground that it does not prevent the development of the spores of several microbes supposed to be pathogenic of important contagious diseases.

If it be admitted that the burning sulphur was properly applied, and that the propagation of the spores is positive proof of persistence of contagion, then the question must be considered as settled, and the practice should be abandoned. But as the first of these propositions, at least, cannot be safely admitted in the attempts at disinfection as commonly practised, and as the method is continued by Boards of Health and hospital authorities as well as in private houses, notwithstanding the evidence against it, it may be useful to re-examine the conditions to be met.

In a given locality there are particles of contagious matter so small as to float in the air, and these settle upon, or become entangled in, all surfaces to which the currents of air carrying them have access. For perfect disinfection the contagious element or virus of all such particles must be so changed as to be no longer contagious. This change must be effected either by physical or by chemical action, or by both acting together.

It seems to be absolutely proven that the one element necessary to the activity of all virus is moisture. Desiccated virus is inactive and impassive; and when desiccation is complete or perfect, as by a sufficient degree of heating for a sufficient length of time, the change is such

* *An Ephemeris of Materia Medica, Pharmacy Therapeutics, &c.* Vol. iii., No. 4.

that the re-supplying of moisture does not reproduce the contagion.

But moisture is an element of varying degree. Too much by dilution may weaken active virus to absolute inactivity, as too little may weaken it to practical destruction.

Contagious matter or virus which is only sufficiently dry to be thus rendered inactive and impassive becomes active by contact with moist surfaces, and thus moisture becomes the essential element in its contagiousness by supplying the conditions under which its molecules can resume the function of propagation or generation. This same element moisture, which is necessary to enable them to propagate contagion, is equally necessary for any reaction with agents which have the power to so change their molecular structure as to destroy their capacity for contagion.

Hence all disinfectants require the presence of moisture, and require it in a degree sufficient to enable all the molecules of contagious matter to commingle and react with the molecules of the disinfectant. If the moisture be sufficient in amount it matters little whether it be held by the virus or by the disinfectant, but the reaction will be much more sure and more prompt if each of the reacting substances be fully saturated with moisture. If either agent be dry or nearly dry, the reaction will be proportionately slow and imperfect.

The condition of the contagious material of an infected apartment, although not absolutely dry, has only the moisture of the common atmosphere, and if there was any such thing in the living animal as a dry surface there could be no infection from such air-dry contagious material.

An air dry disinfectant or antiseptic is equally inactive and impassive, and for the same reasons; namely, the absence of the physical and chemical conditions for reaction.

When sulphur is burned in air a dioxide of sulphur is formed. One atom unites with two atoms of the oxygen of the air to form an anhydrous or perfectly dry gas which occupies practically the same space as did the oxygen combined. This sulphur dioxide is therefore a heavy gas, and as it cools after being formed by the combustion, it falls, so that any enclosure in which it is formed will fill up from the bottom as it would with water, and but for the laws of diffusion of gases, an enclosure might have the pure gas at the bottom and none at the top. The laws of diffusion, and the currents of air and gas caused by the heat of combustion, do, however, carry the gas to all parts of an enclosure, and yet the gas is in greatest proportion near the floor, and any leakage there, as under the doors for example, will waste much more gas than the same openings higher up.

The sulphur dioxide formed is a perfectly anhydrous or dry gas, and is therefore called sulphurous anhydride. It is not an acid, but is an indifferent, inactive, impassive gas, showing but a feeble tendency to combine with anything, or to exert any power. It has a moderate affinity for moisture, and when one molecule of the gas combines with one molecule of water sulphurous acid is formed; when combined with more than one molecule of water a liquid sulphurous acid is formed of a strength proportionate to the amount of water. This solution of sulphurous acid is commonly called simply sulphurous acid, and as found in the markets it commonly contains from 3 to 6.5 p.c. of true sulphurous acid, or the compound molecule made up of one atom of sulphur, two atoms of oxygen, and one molecule of water. This sulphur dioxide, or sulphurous anhydride plus water, or sulphurous acid, unlike the inactive dioxide, is a very active and very potent substance, and its prominent characteristic is its affinity or appetite for oxygen, by which it is converted into sulphuric acid. This affinity for oxygen by which it takes that element from all its looser combinations, makes it a powerful deoxidising agent. And, by taking oxygen away from its looser combinations in the infective matters, it

breaks up their complex molecules, destroys their power of contagion, and thus becomes disinfectant. Again, instead of taking away oxygen from compound molecules it may unite with this oxygen and thus form sulphuric acid as a new component of the compound molecule, changing this so as necessarily to destroy it and therefore be disinfectant.

All this detail is to show that sulphur dioxide, resulting from burning sulphur in the air, is not a disinfectant, but requires the presence of moisture either with the sulphur dioxide, or with the infected matter, or with both. And, further, that in proportion to the amount of moisture up to what would be a very large dilution, the more there is present the more perfect are the conditions for thorough disinfection, and the less moisture there is present the more imperfect the disinfection.

Now, if the practice of Boards of Health and other authorities be examined, it seems to be very defective indeed, unless they use an abundance of watery vapour without thinking it worth while to mention it in their directions and practice.

The common usage seems to be to close up the infected apartments as thoroughly as practicable and to burn sulphur in them in the proportion of four pounds of sulphur to each 1000 cubic feet of space.

There are no directions to stop up the lower chinks more carefully than the upper ones, while the lower half of a door will waste twice as much gas as a window. The sulphur is usually put in an iron pot or pan, and this is set in a larger vessel of water or upon a vessel of wet ashes or sand; and this seems to be done to lessen the risk of fire rather than to supply vapour of water. The sulphur is lighted by means of alcohol poured upon it and lighted, and the apartment is then closed and watched until the sulphur is burned out. The dioxide formed finds a little moisture in the normal atmosphere of the room, and thus a small proportion of it gets converted into the active sulphurous acid. Then the heat of the burning sulphur vapourises a portion of the water in the vessel in which it is placed. Under favourable conditions the amount of water thus vapourised may equal or slightly exceed the weight of the sulphur burned. But under general conditions it will be much less. These two sources being the only ones from which moisture is supplied, and the amount supplied being very much too small, it is only reasonable that the disinfection should be proportionately incomplete, and under such conditions any condemnation of sulphurous acid as a disinfectant is unsound and irrational.

The conditions for a much better application of this agent are very easily supplied. To fumigate with the active sulphurous acid, instead of the inactive dioxide of sulphur, it is only necessary to evaporate water to the extent of three or four times the weight of the sulphur burned, or to wet the surfaces to be disinfected, or both, so that plenty of moisture may be present during the burning of the sulphur. A shallow pan of water upon a kerosene stove well started in advance of lighting the sulphur, and the floor, ceiling, and walls well sprinkled with water by means of an ordinary dust-brush, is perhaps as good a practice as any.

There is abundant evidence on record that sulphurous acid in small amount is destructive to all the lower orders of animal and vegetable life, to all fermentations both vital and chemical; and, all that the more recent elaborate investigations seem to have shown is, that the spores or germs of certain microscopic organisms were not destroyed by it as applied to them, even in the presence of abundant moisture in some of the trials. Many of the late investigations have been made with very great care and labour and by modern accurate methods. Some of the best results are, however, confusing, if not contradictory, and, therefore, are inconclusive, even in regard to the resistances of spores.

Chiefly from the above-mentioned considerations the writer reaches the conclusion that burning sulphur for

disinfection should by no means be abandoned, but should be more thoroughly and more carefully applied.

Not only in diphtheria, but in all infectious diseases, some such disinfectant is greatly needed in preventing the spread of disease, and diminishing the risks of susceptible persons, and no other method has yet been proposed that is more effective, more simple, or of easier application.

In the less convenient and more costly method of disinfecting by gaseous chlorine the same principles apply, and the same conditions are necessary. Dry chlorine gas is as inactive as sulphur dioxide, and from deficient supply of moisture the one will fail as often as the other.

When chlorine is generated from common salt by means of dioxide of manganese and sulphuric acid, the salt and manganese are commonly mixed into a thin paste with water before the acid is added. Then on adding the acid much heat is developed, and a proportionate amount of water is evaporated and disengaged with the chlorine. But this amount of water is far too small for the full effect of all the chlorine, and unless all the surfaces be well wetted, and steam be supplied, the disinfection will be defective.

If the walls and ceilings of apartments be kalsomined, or be covered with any other preparation of glue or paste, these should be scrubbed off clean with hot water before the disinfection, because disinfection does not destroy the tendency to putrescence in gelatin, glue, paste, &c.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, September 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined, one was found to be "very slightly turbid," viz., a sample collected on the 1st ultimo, the remaining 174 samples being clear, bright, and well filtered.

The generally satisfactory character of the water supply during the month of August is well indicated by a comparison of the mean and maximum proportions of organic carbon found in the Thames-derived waters distributed to the Metropolis during the months of June, July, and August, respectively, thus:—

	Means.	Maxima.	
June	0.150	0.166	} Parts per 100,000.
July	0.152	0.185	
August	0.150	0.175	

But just as the numbers for July were somewhat heightened by the occurrence during the latter part of the month of a flooded state of the rivers, brought about by the unprecedented rainfall of the 17th of July, so were the numbers for August similarly heightened by the persistence, during the early part of the month, of the previously brought-about floods, sustained as they were by a considerable rainfall in the weeks following that of the above-mentioned wholly exceptional fall.

The proportion of organic matter present in the water, as determined alike by the estimations of organic carbon found and of oxygen consumed, though affected sufficiently to render analyses made on an early day in the month no fair criterion of the character of the month's supply, was, nevertheless, influenced by the floods, but to a very inconsiderable extent only, as noted also in our previous monthly report. The degree of colour-tint of the water, however, when viewed through a thickness of two feet, was found to be more appreciably affected. Thus, while the mean ratio of brown to blue tint of the Thames-derived water was, during the first half of the month of August as 20 : 20, it was found during the last half of the month, after the subsidence of the floods, to be only as 14.1 : 20.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE DRY ASSAY OF TIN ORES.* PART I.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Continued from p. 104).

(3). In assaying ores in the dry way, it has been, and still is, very common to give a salt cover. To try what effect this would have, the foregoing two sets of experiments were repeated, adding the salt.

It was found that the charges melted less rapidly and were not so thin as before; when cold, the surface of the slag was uneven and rough; the crucible was corroded, but less soaked with potassium cyanide, the upper part showing no prills of tin. The slag showed a very coarsely granular structure; it was opaque, milk-white, but somewhat dull in comparison with that of the pure cyanide. No other differences were observable.

The low results shown by the averages were startling. They could not be attributed to any action of the sodium chloride, nor to the small amount of silicate derived from the corrosion of the crucible. The salt was examined, and found to be rich in sulphuric acid; this explained the loss in tin (see Table XVI.). Fine Michigan table-salt was then tested, and sulphuric acid found to be present here also; therefore, nothing further was attempted with salt. No special advantage is apparent in its use with potassium cyanide, as the slags are thinner without it, and form a better "wash" for the sides of the crucible than the less readily fusible salt. If it is to be used at all, recourse must be had to Ohio salt, which, according to the Report of the Geological Survey of Ohio, "Economic Geology," 1888, vol. vi., p. 663, is free from sulphates, while Michigan salt always contains them.

(4). Ricketts recommends the chalk-lined crucible for the assay with potassium cyanide. He gives the charge, 10 grms. of ore and 40 grms. of potassium cyanide, with half of the flux in the bottom of the crucible and the other half mixed with the ore, then the usual cover of cyanide,

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 2.

TABLE IX.

No. of Assay.	Resulting Tin.							
	Total.		In button.		In slag.		In crucible.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
39.	6'752	67'52	6'685	66'85	—	—	—	—
40.	6'752	67'52	6'685	66'85	—	—	—	—
41.	6'752	67'52	6'685	66'85	—	—	—	—
42.	6'742	67'42	6'675	66'75	—	—	—	—
Average..	6'749	67'49	6'682	66'82	0'060	0'60	0'007	0'07

TABLE X.

No. of Assay.	Resulting Tin.							
	Total.		In button.		In slag.		In crucible.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
43.	3'266	65'32	3'200	64'00	—	—	—	—
44.	3'231	64'62	3'165	63'30	—	—	—	—
45.	3'226	64'52	3'160	63'20	—	—	—	—
46.	3'176	63'52	3'110	62'20	—	—	—	—
Average..	3'225	64'49	3'159	63'17	0'020	0'40	0'046	0'92
47.	6'505	65'05	6'430	64'30	—	—	—	—
48.	6'405	64'05	6'330	63'30	—	—	—	—
49.	6'235	62'35	6'160	61'60	—	—	—	—
50.	6'220	62'20	6'145	61'45	—	—	—	—
Average..	6'341	63'41	6'266	62'66	0'065	0'65	0'010	0'10

TABLE XI.

No. of Assay.	Resulting Tin.							
	Total.		In button.		In slag.		In crucible.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
51.	6'648	66'48	6'625	66'25	—	—	0'017	0'17
52.	6'618	66'18	6'595	65'95	—	—	0'017	0'17
53.	6'458	64'58	6'435	64'35	—	—	0'017	0'17
54.	—	—	—	—	—	—	—	—
Average..	6'574	65'74	6'551	65'51	0'006	0'06	0'017	0'17

TABLE XII.

No. of Assay.	Resulting Tin.							
	Total.		In button.		In slag.		In crucible.	
	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.	Grms.	Per cent.
55.	3'223	64'46	3'100	62'00	—	—	—	—
56.	3'202	64'04	1'310	26'20	1'892	37'84	See slags.	See slags.
57.	3'198	63'96	3'075	61'50	—	—	—	—
58.	3'198	63'96	3'075	61'50	—	—	—	—
Average..	3'205	64'11	—	—	0'033*	0'66*	0'090*	1'80*

* Except No. 56.

to which is added a salt cover, and heats for fifteen minutes. These directions were followed, only omitting the salt cover.

It was expected that the chalk-lining would at least partly prevent the cyanide from filtering into the crucible, but no difference could be observed, the crucible being just as black as if it had had no chalk-lining.

The structure of the slag was slightly coarser; it was more uneven in fracture, and of a bluish grey colour, instead of the usual pure milk-white.

The average of the results is 2'1 per cent lower than that obtained by the chemical analysis, and 1'75 per cent lower than the average of the corresponding 10-grm. assays, Nos. 39 to 42. The separate assays also show a difference of 1'9 per cent, which is very unfavourable. The first reason for this that suggested itself was the possible presence of gypsum in the chalk, but no sulphates

were found. There remains, therefore, only the presence of lime to account for the slagging of tin.

By a mistake in assay No. 54, the entire 40 grms. of potassium cyanide were mixed with the 10 grms. of ore, and charged with it. No button whatever was obtained. The bottom of the crucible was covered with a spongy, greenish grey mass, and this by the ordinary white slag of potassium cyanide. This shows the necessity of having a good layer of potassium cyanide on the bottom of the crucible, probably on account of the tendency the tin has not to collect in a single button. If the crucible is filled with a uniform mixture of ore and cyanide, a number of small buttons will be produced mixed with the slag. If a layer of pure potassium cyanide cover the bottom of the crucible, the particles of tin will sink into it, and form on the undisturbed bottom a nucleus, around which other particles can collect, and thus take up gradually most of

the tin. The effect is similar if charcoal be mixed with the potassium cyanide (see 5 to 7).

(5). The regular method of assay with potassium cyanide was modified in the same way as the German method; i. e., the stannic oxide was first reduced by charcoal, and the potassium cyanide then added to collect the particles of metallic tin into one button. It was expected that the iron would be taken up by the potassium cyanide instead of alloying with the tin. The result was tested by dissolving the slag in water, filtering the solution, acidulating the filtrate with hydrochloric acid, and boiling to expel the hydrocyanic acid formed. It was then tested with a mixture of ferrous and ferric salt, which gave the reactions for potassium ferro- and ferri-cyanide. Another part of the filtrate was evaporated to dryness, treated with nitro-hydrochloric acid, again evaporated to expel all cyanogen, and taken up with hydrochloric acid. On adding ammonium hydroxide, the reddish brown ferric hydroxide was precipitated, showing again the presence of iron.

In the experiments, 5 grms. of ore were mixed with 1 grm. of charcoal, placed in a naked crucible, size F, and heated for a quarter of an hour after the charge had become dark red; then 20 grms. of potassium cyanide were added; after this, thirteen minutes were required before quiet fusion was obtained.

The slags had the usual characteristics of the pure cyanide, but black patches of carbon were irregularly dispersed through them. The buttons were white, very bright, malleable, and free from iron; they were, however, rough, and covered with bead-like excrescences of tin.

These results are very unsatisfactory. The average gives 3.73 per cent less tin than is present; it is 3.20 per cent lower than that of the corresponding 5-grm. assays, Nos. 35 to 38, and 2.21 per cent lower than that of the modified German method, Nos. 23 to 25. On comparing the separate weights of the tin buttons obtained, it will be seen that the tendency of the tin not to collect in one button is enhanced by the presence of the charcoal with which the ore had been mixed. The only result of positive interest obtained by the experiments is the fact that the iron of the black tin, reduced to the metallic state, goes into the slag, and not into the button, as in the modified German assay.

Similar experiments carried on in a charcoal-lined crucible were equally unsatisfactory.

(6). The same method, only using a porcelain crucible, bears the name of Levol's method. Kerl* and Balling† give it as follows:—2 grms. of ore are mixed with 20 per cent of charcoal in a porcelain crucible, and heated for from fifteen to thirty minutes in a muffle; 0.50 to 0.75 grm. of potassium cyanide is added, and the heating continued another five minutes. They say that the results are accurate to from 0.3 to 0.5 per cent.

It was found that it is necessary to grind ore and charcoal very fine, and that an excess of charcoal must be avoided.

Two grms. of ore were mixed with 0.5 grm. of charcoal, and heated for half an hour in the muffle at a good scorification temperature. The crucibles were then removed, allowed to cool, 1 grm. of potassium cyanide added, and the crucibles returned to the muffle for ten minutes.

They were all blackened and somewhat corroded; the slag was of a light grey colour, from the charcoal, and there was a small amount of green slag. In none of the assays had the tin collected in one button; it varied in size from a button down to a fine grey powder. The crucibles were now placed in hot water, the small buttons picked out, and the fine tin separated from the charcoal and insoluble green slag by washing. This is the uncertain part of the assay. The fine tin separates with difficulty from the green slag. If this is entirely removed, some tin will be lost, and the resulting weight will be too

low; if all the tin is recovered, some slag remains with it, and the result is too high. Thus the assayer must choose between two evils, and this causes a feeling of uncertainty. Any slight mistake is multiplied by fifty when the result is expressed in percentage. This is illustrated in Table XIII.

TABLE XIII.

No. of Assay.	Resulting tin.	
	Grms.	Per cent.
59.	1.350	67.50
60.	1.335	66.75
61.	1.305	65.25
Average	1.330	66.50

The average is too low, showing loss from excessive care in washing to obtain pure tin. The greatest discrepancy between the single results is 2.25 per cent. This shows how difficult it is to effect a satisfactory separation of fine insoluble slag and fine tin. During the past two years the writer has made a number of assays according to this method. The results obtained from duplicate assays only agreed well when all the tin had collected in one or more large buttons; they were never satisfactory if the tin was present in the form of fine powder. It was not discovered why in one case a button, in another a powder, should be obtained. The statement made by Kerl and Balling, that the results of this method are accurate within 0.5 per cent, needs modification, as it certainly does not apply to all tin ores. Probably those of the Black Hills contain impurities that were not present in the ores Kerl and Balling have reference to.

(7). The last experiments made with potassium cyanide followed T. W. E. David, in his "Report on the Geology of the Vegetable Creek Tin-Mining Field," Sydney, New South Wales, 1887, p. 153. Mr. David says that at the Glen Smelting Works at Tent Hill the potassium cyanide is mixed with charcoal. The only reason that can be brought forward for this modification is, that the potassium cyanide used must have been very impure. Thus, in order to increase its reducing power, charcoal was added.

Five grms. of ore were fused with a mixture of 30 grms. of potassium cyanide and 1 grm. of charcoal; only two-thirds of the flux were mixed with the ore, one-third being rammed into the bottom of the naked crucible.

Contrary to expectation, the charge fused as readily as if it contained no charcoal, and came very quickly to a quiet fusion. On breaking the crucible, no button was to be found, but only fine prills of tin disseminated through a pumice-like dark grey slag, containing irregular streaks coloured black by carbon. This shows again the necessity, alluded to above, of having in the bottom of the crucible a layer of pure potassium cyanide for the reduced particles of tin to collect in and form a button.

In the preceding experiments, the ordinary c. p. potassium cyanide was used, as it seemed important that the results obtained should be based on a reagent whose composition was definitely known. But this pure cyanide is somewhat expensive (1.90 dollars a pound), and to see whether its use was absolutely necessary, the different commercial grades were tested. First, however, c. p. cyanide was mixed with cheaper fluxes, such as pure potassium and sodium carbonate, to obtain, if possible, a flux which would have the same action as the pure cyanide, but be considerably cheaper. The effect produced by potassium sulphate was also investigated.

(To be continued).

Determination of Starch Granules in Corn.—Z. v. Mikowski.—The author concludes that the methods of Aeböth and Marcker both give good and accordant results. In determinations of sugar either the gravimetric process of Allihn or the volumetric method of Soxhlet should be used, as the process of Reischauer gives merely approximate results.—*Zeitschrift für Analytische Chemie*, Vol. xxix., Part 2, 1890.

* "Metallurgische Probirkunst," 1882, p. 483.

† "Die Probirkunde," 1879, p. 392.

THE FIXATION OF ATMOSPHERIC
NITROGEN.*

PART II.

By A. A. BRENNEMAN, S.B.†

Continued from p. 103.)

An Inquiry in Regard to the Conditions under which Cyanogen is Produced by Direct Union of Nitrogen and Carbon.

THE union of nitrogen with other chemical substances is brought about with so much difficulty that it has long been the custom to speak of nitrogen as an inert substance showing little affinity for or tendency to combine with other elements, yet the very large classes of compounds in which nitrogen is an essential element show that it is not difficult to retain it in a compound once formed, or to hand it over from one compound to another in the reactions by which chemical compounds are formed or decomposed. The difficulty, then, is simply that of getting free nitrogen, as it exists in the air, to enter into direct combination with any other element, and this difficulty is so real and serious that, practically, all of the nitrogenous compounds used in the arts are obtained by the decomposition of other nitrogen compounds. Free nitrogen is one of the most abundant substances on the earth, and combined nitrogen is essential to some of the most valuable of commercial products, but the ready fixation of the nitrogen of the air on a manufacturing scale in any single compound which may be used as the starting point of a series of substances derived from it, has yet to be accomplished.

This indifference to combinations, together with the considerable degree of permanence given by nitrogen to the compounds into which it enters, lead to the conclusion that a certain quantity of work, represented by a certain quantity of heat, has to be done in order to bring free nitrogen to the condition in which combination is possible. The chemist explains this by saying that the condition of free nitrogen is that of two atoms joined to one another to form a molecule and requiring the expenditure of a certain quantity of heat to tear them apart and leave each atom free to enter into new combinations.

The most prominent source, perhaps the only true source, of nitrogenous compounds in nature is found in the union of nitrogen and oxygen of the air under the influence of the electric discharge, as in lightning, &c. Nitric acid is washed down from the air by rain during a thunderstorm, either free or as ammonium nitrate or nitrite, and these substances, and ammonia, the product of their reduction, are the starting points of mineral, vegetable, and animal compounds containing nitrogen. The conversion of nitrogen of animal and vegetable matter into ammonia and nitric acid under the influence of bacterial life is a secondary process and does not deal with free nitrogen.

Whether the union under the influence of the electric spark be purely a heat effect, or whether it results in part from a special polarity impressed upon the atoms of nitrogen by the discharge, it is now definitely proven that heat alone in presence of a strongly basic substance, like an alkali, is sufficient to effect the combination of nitrogen and carbon. The discovery, made accidentally, that the hot blast iron furnace fulfils at times the conditions necessary for the production of cyanogen from nitrogen of the air, was the beginning of a series of experiments upon the fixation of free nitrogen which have cast much light upon the nature of the problem.

Nevertheless, the conditions of the blast furnace furnish the best basis for the study of the question, and most of the early attempts to fix atmospheric nitrogen as cyanogen

have striven to imitate these conditions more or less closely. Bunsen indeed (*ante*) suggested the construction of a furnace on the plan of the blast furnace for production of cyanides only, but it is difficult to see the practicability of such a plan unless the size of the furnace were very much reduced or the yield of cyanides very small as compared with consumption of fuel. We have to inquire, then, what are the essential and what the non-essential conditions for the fixation of free nitrogen as cyanogen? The investigations of the blast furnace itself with this object has been done by Bunsen and Playfair (*ante*), and the various forms of apparatus which have been applied to the manufacture of cyanides upon this plan and the experience drawn from them furnish much additional material for such an inquiry.

We are limited here to the study of the synthesis of cyanogen, but the conversion of the nitrogen of the air into ammonia or cyanogen on the one hand, or into an oxide of nitrogen on the other, are mere phases of the great question of the fixation of nitrogen, and as the synthesis of one of these substances by the aid of atmospheric nitrogen would lead to the production of all, this limitation cannot exclude all considerations of these related substances.

The conditions essential to the fixation of nitrogen and the production of cyanides are indicated in the operation of the blast furnace, but only in the most general way. Neither observations nor experiment with the blast furnace have yet enabled any one to control it for the production of cyanides. The appearance of cyanides as a product of these furnaces, whenever observed, has occurred unexpectedly and has generally ceased as suddenly and mysteriously as it began. Bunsen's proposal, to erect a furnace similar to a blast furnace to be worked for cyanides only, has never been fully acted upon, and in the light of present experience it offers little promise of success. We have learned from the study of the blast furnace only that a high temperature, a reducing atmosphere, an alkaline flux, and an excess of nitrogen are conditions favourable to the process.

The conditions most suitable in respect to temperature, flow of nitrogen, quality and density of carbon or carbonaceous fuel, proportion and nature of base, &c., are as yet undefined.

The more manageable furnace of Possoz and Boissiere (*ante*), although holding rather closely to the principle of the blast furnace, is free from its greatest defects, in that it has no very deep column of coal to resist the flow of gases or crush the lower portions into a compact mass by its weight. The air or nitrogen is admitted at many points also, and the cross section of the furnace is not small enough to prevent access of the gases to the centre of the column of coal. Its defects are, slowness of conversion of nitrogen into cyanogen, rapid destruction of the lining of the furnace, and contamination of the cyanides with silicates thereby formed.

The process of Margueritte and Sourdeval (*ante*) and that of Romily (*ante*) are each, for a different reason, free from the chief of these defects, yet they have been no more fortunate than their predecessors in finding a practicable, commercial process.

In order to reach a conclusion as to the present aspect of the whole question, it may be well to take up and consider in detail the various conditions upon which the absorption of free hydrogen by carbon depends, to see how far the theory of chemistry may lead us in anticipating the effect of each, and to find, if possible, what combination of conditions gives, in the light of theory and past experience, most promise of success.

1. *The Influence of Temperature.*—Possoz and Boissiere (*ante*), to whom great deference is due as the authors of the most persistent as well as the most successful efforts ever made in this field, give unqualified testimony, as the result of long experience, to the necessity for very high temperatures. A white heat is said to be required, and the fixation of nitrogen, other things being equal, is

* *Journal of the American Chemical Society*, vol. xi., Nos. 1-2.

† The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

directly proportional to temperature. On the other hand, Armengaud and Ertel both claim that lower temperatures are quite adequate to effect the combination of nitrogen and carbon. Walter Weldon, also, one of the foremost authorities in the application of chemistry to manufactures of this or of any age, stated, in 1879, as the result of his own experiments, that the limit of temperature in this operation had been placed too high and that a red heat was sufficient. Siepermann, in 1887, testified to the same effect, basing his views on a series of experiments.

The question at issue relates only to the difference between a cherry red and a white heat, but this difference is of the utmost importance in the practical operation of a plant, and may of itself be the point upon which the whole question will ultimately turn. It is possible, however, that, under conditions, either of the above views may be correct, and the question must remain an open one until the process shall have been more fully studied.

2. *The Influence of Oxygen.*—It is generally admitted as the result of all experiments upon the manufacture of cyanides, that oxygen and cyanogen cannot exist together at high temperatures. Theory leads to the same conclusion. Cyanogen is a combustible substance, and the effect of oxygen upon cyanides is either, in the case of the alkaline cyanides, to convert them, first into cyanates and then into carbonates, or in the case of cyanides of the heavy metals, to decompose them with liberation of carbon monoxide and dioxide. All processes, therefore, using air as a source of nitrogen provide for absorption of oxygen or its conversion into oxides of carbon. The mixed gases of the cyanogen furnace must be as a whole reducing, not oxidising, in character.

3. *The Influence of Water.*—Here again we have P. and B. (*ante*) with their weight of practical experience insisting upon a condition which receives little support from others. It is evident, however, that the conditions of their furnace did not prevent the exclusion of moisture to such an extent as to decide the question absolutely, and the ill effects of water when admitted purposely and in greater quantity may be ascribed, in great part, to its cooling effects merely, when we remember the great expenditure of heat under which water is decomposed by carbon. Water in excess, also, decomposes cyanides, yielding ammonia. The experiments of Langlois are quite conclusive as to the principle that water in moderate quantity does not influence the production of cyanides, and Armengaud, Ertel, and others (*ante*) speak positively as to its advantages. If the formation of ammonia is a preliminary stage in the synthesis of cyanogen, as Kuhlman suggests (*ante*), the presence of hydrogen, or, what is in effect the same, of vapour of water, is a necessary condition. Vapour of water is an oxidising agent under certain conditions of temperature and for certain elements, but it is possible that cyanogen is not attacked by it at high temperatures in presence of hot carbon, carbonic oxide, or hydrocarbons. The conclusions of several experimenters that water does not hinder the formation of cyanides is not, at any rate, definitely contradicted by theory.

4. *Time of Contact between Nitrogen and Carbon and Degree of Subdivision of Carbon.*—If we assume that the base, which is found to be necessary in production of cyanogen from nitrogen of the air, combines instantly with the nascent cyanogen, the question of time is one simply of the speed of the preceding reaction between nitrogen and carbon. Chemical action between a solid and a gas, when the temperature necessary for the reaction has been attained, depends principally upon the surface exposed. The action may be assumed to be instantaneous, like the action of oxygen upon hot and finely divided carbon, and to be retarded only because the products of combustion cannot be removed from the sphere of action at the same rate at which the action takes place.

In a process like that of Possoz and Boissiere, and when each fragment of charcoal is bathed in a film of fused potash, action is limited by the rate at which the fused cyanide circulates in the pores of the charcoal and gives

place to unchanged potash on the surface. New surfaces of carbon for attack, or of potash for absorption, are therefore exposed less frequently than is required, and complete saturation, that is, conversion into cyanide, is attained only after a long exposure and with much waste of gas and heat. The absorption of nitrogen is probably also retarded progressively as combustion proceeds, both because the pieces of carbon are reduced in size and therefore facilitate clogging of the flow of gas, and because the potash and fused cyanide are relatively more abundant as carbon decreases and lesser surface of carbon is exposed.

Both practice and theory, therefore, lean to the conclusion that, other things being equal, the process will be hastened by any arrangement that tends to increase the surface of carbon exposed. The use of pulverised fuel would seem to be the ideal condition so far as carbon is concerned, and with an excess of ammonia, the only gaseous alkali, would probably, at a proper temperature, yield ammonium cyanide readily, as shown in Romilly's experiment (*ante*), in which a smoky flame of hydrocarbon gas burning in air yields ammonium cyanide when the gas is charged with ammonia.

The effect of supplying the base also in the condition of powder would probably be to still further facilitate the action, as gaseous cyanogen would meet solid particles of highly heated base as soon as formed, and would combine with the metals of these bases to form cyanides. Alkalies would fuse and would probably tend to produce aggregations with particles of carbon, to that extent impeding access of air to them, but when we take into account the increased rapidity of chemical action under these conditions and the short time given to each group of particles in passing through the furnace, the gain by the process of pulverising will probably be greater than the loss. Solid bases, like lime or baryta, are free from the latter objection, but also have less chemical energy.

5. *Influence of Alkalies or Other Bases.*—The influence of a base upon the union of carbon and nitrogen, both being in contact with the base and at a temperature sufficiently elevated for combination to occur, is probably due merely to the fact that the base serves to remove cyanogen from the sphere of action as fast as it is formed. The belief in a predisposing affinity, a non-correlated power, acting from a given centre to bring about a reaction in which the predisposing body has no share except to combine, *subsequently*, with the products of the reaction, is an ingenious fiction of the older chemistry, which finds little support at the present time. The influence of a foreign substance in impeding the union of two bodies by lessening the opportunities for contact of their respective atoms within a given time supplies a more tangible explanation. Every chemical reaction is limited in violence after the first moment of action—is impeded and finally checked—by the products of the reaction, unless these are removed. Like any foreign substance these substances impair the freedom of access of the reacting atoms to one another and absorb heat which is necessary to the reaction. Whatever tends to remove these products quickly from the field of action tends to facilitate the reaction itself. When *a* and *b* unite to form *ab*, the presence of a third substance, *c*, capable of combining with the compound *ab* to form *abc*, but not with *a* or *b* separately, will facilitate the union of *a* and *b*, for the above reasons.

This would seem to be the function of the alkali or other base in the synthesis of cyanogen. The conclusion is sustained apparently by the experiment of Langlois and the earlier chemists (*ante*), in which ammonia passed over hot charcoal yields ammonium cyanide. Trommsdorff first suggested that it was the presence of ammonia that favoured here the formation of cyanogen by furnishing a means of fixing it as soon as formed.

The theory of the action of bases, of alkalies at least, is susceptible of another explanation. Many authorities (Bromeis, Bunsen and Playfair, Graeger, Rieken *et al.*, *ante*) believe that the union of carbon and nitrogen occurs only at or above the temperature at which potassium is

reduced from its oxide by carbon. Metallic potassium or its vapour must be taken into account upon this hypothesis when the reaction in question is studied. This view would explain the lesser activity of soda in forming cyanides, as it is less readily reducible. Graeger (*Zsb. chem. Tech.*, 1858, 81) finds that in the old fusion process for prussiates the yield is lessened in proportion as potash is replaced by soda, even at temperatures approaching the fusion point of the cast iron pot. He believes that nitrogen from the organic matter in this case is volatilised and lost before metallic sodium is formed, owing to the high temperature required for reduction of sodium. Lime and baryta, from their infusibility, are also difficult to reduce, and should be less suitable for the process. Knowing the incompatibility of cyanogen and oxygen at high temperatures and the fact that cyanogen unites directly with the metals, it is quite possible that cyanogen can only combine when the metal itself is presented to it, and cannot reduce the oxide, at least only by being itself destroyed. Bunsen and Playfair held (*ante*) that cyanogen in the upper part of the iron furnace acted as a reducing agent and was itself destroyed in reducing oxides of iron.

The theory of Berthelot (*ante*) is interesting in this connection. He holds that a direct compound of potassium and carbon (C_2K_2) is formed, and that this compound absorbs nitrogen, forming with it potassium cyanide. The theory is in perfect accord with the preceding one. Delbrück (*ante*) has also shown that cyanogen is formed when a mixture of nitrogen or ammonia with carbon dioxide is brought in contact with fused potassium.

It is possible also that potassium or other metal, under these conditions, unites directly with nitrogen to form nitrides, which then combine with carbon, yielding cyanides. The observation of Briegleb and Geuter, already referred to (*ante*), that magnesium nitride, when heated with carbonic oxide or carbonic acid, evolves cyanogen, lends colour to this view.

6. *The Nature of the Base to be Used.*—As far as experiments have gone, potash seems to be the base best suited. Its great chemical energy and ready fusibility and reducibility in presence of carbon give it advantages over all other bases. Soda, besides being somewhat less powerful as a base, fuses at a higher temperature and therefore involves increase of wear and cost in apparatus. On the other hand, it is cheaper, weight for weight, than potash, and, in addition, its lower molecular weight enables it to do more work for a given weight than potash in the proportion of 138:2 to 106.

The facility with which ammonium cyanide is formed when ammonia is passed over hot charcoal indicates that ammonia, like the fixed alkalies, combines very readily with cyanogen. It has the advantage of not acting as a flux upon the material of the furnace. The use of ammonia, itself produced from nitrogen of the air, to facilitate the synthesis of cyanogen at a lower temperature than that thought necessary for cyanogen alone, is suggested by Komily's experiment and may be a feature of future development in the fixation of nitrogen.

Of the infusible bases the alkaline earths, lime, baryta, strontia, and magnesia only, seem to have sufficiently strong basic power to form cyanides with the air. The cyanides of other metals decompose quite readily when heated. The advantages of the alkaline earths are their infusibility, which prevents clogging of the mixture of coal and basic substance and so permits perfect access of nitrogen, and their cheapness. The corresponding cyanides are soluble and easily converted into alkaline cyanides. These qualities compensate to some extent for the deficient chemical energy of the alkaline earths. Margueritte and Sourdeval (*ante*) found that baryta absorbed nitrogen rapidly and that barium cyanide yielded ammonia on treatment with steam. Siepermann (*ante*) mixes baryta with alkalies to prevent fusion and clogging. Lime, the cheapest of these bases, seems to have been little used. Armengaud speaks of using it in his apparatus in 1843 (*ante*) and Fleck (*ante*) claimed the discovery that

hot calcium hydrate could convert a mixture of nitrogen and carbonic oxide into ammonia and carbon dioxide.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 19th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

(Continued from p. 109).

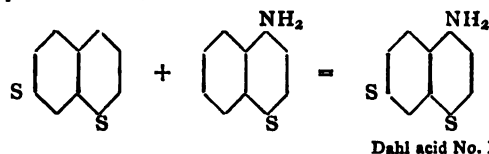
59. "*Studies on the Constitution of the Tri-derivatives of Naphthalene.* No. 4. *The Constitution of α -Naphthylaminedisulphonic Acid* Dahl No. II. *Naphthalene-1:2'-disulphonic Acid.*" By HENRY E. ARMSTRONG and W. P. WYNNE.

When naphthionic acid is sulphonated with 35 percent anhydro-sulphuric acid at a temperature not exceeding 30° according to Dahl and Co.'s German patent No. 41957, 1886, two disulphonic acids are produced, which are respectively known as α -naphthylaminedisulphonic acid No. II. and No. III., the latter constituting the chief product. The constitution of acid No. III. has been given in a previous communication (*Proc. Chem. Soc.*, 1890, 16). With the object of comparing the disulphonic acids obtained by the sulphonation of α -naphthylamine with those known to be produced by the sulphonation of α -naphthol, the authors have undertaken the investigation of acids Nos. I. and II. of Dahl and Co.'s patent, and are now in a position to communicate the results obtained by the examination of acid No. II., for a liberal supply of which they are indebted to Messrs. Dahl and Co.

The product received was in the form of potassium salt, and appeared to be uniform; but on investigation it was found to contain a noteworthy quantity, perhaps 20 percent, of an α -naphthylaminetrisulphonic acid, the formation of which under the conditions above named, is especially interesting as throwing further light on the process involved in the production of isomeric disulphonic acids. When reduced by the hydrazine method, this α -naphthylaminetrisulphonic acid yields a *naphthalenetrisulphonic acid* characterised by forming a chloride, $C_{10}H_5(SO_2Cl)_3$, which crystallises from a mixture of benzene and petroleum spirit in small prisms melting at about 191°; whilst by the Sandmeyer method it is converted into a *chloronaphthalenetrisulphonic acid* characterised by forming a chloride, $C_{10}H_4Cl(SO_2Cl)_3$, which crystallises from benzene in minute prisms, from a mixture of benzene and petroleum spirit in small crystalline aggregates, and from acetic acid in small scales melting at 215°.

α -Naphthylaminedisulphonic acid No. II. on conversion into naphthalenedisulphonic acid by v. Baeyer's hydrazine method, yields a new acid, the salt of which will be described in a subsequent communication. The chloride of this acid, $C_{10}H_6(SO_2Cl)_2$, crystallises from benzene, in which it is readily soluble, in prismatic forms; from a mixture of benzene and petroleum spirit in tufts of opaque irregular needles; and from acetic acid in beautiful glistening plates; it melts at 122.5°, and on distillation with PCl_5 yields a dichloronaphthalene melting at 63–63.5°, convertible by sulphonation, &c., into a sulphochloride, crystallising in needles, which become opaque and melt at 117°. The acid is consequently the 1:2'-disulphonic acid, and is the sixth known naphthalenedisulphonic acid. By the Sandmeyer method, acid No. II. can be converted into a chlorodisulphonic acid, the chloride of which crystallises from a mixture of petroleum spirit and benzene in minute needles, and from acetic acid in small prisms; it melts at 126–127°, and, on distillation with PCl_5 , yields 1:4:3'-trichloronaphthalene,

characterised, among other properties, by melting both at 56° and 66° under the conditions already described (*loc. cit.*). Superposing these results, it follows that α -naphthylaminedisulphonic acid Dahl No. II. is, as its mode of formation would seem to indicate, a sulphonated naphthionic acid, and that it has the constitution:—

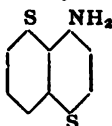


Dahl acid No. II.

The authors reserve the investigation of the properties of the 1:2'-naphthalenedisulphonic acid and its derivatives.

60. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 5. The Constitution of the Schöllkopf α -Naphthylaminedisulphonic acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

The formation of the Schöllkopf α -naphthylaminedisulphonic acid (German patent 40571) by the nitration and subsequent reduction of the authors' naphthalene-1:4'-disulphonic acid (Bernthsen, *Ber.*, 1889, 3327) renders it evident that the generally accepted view of the constitution of this acid is a correct one. Having been favoured by the Actiengesellschaft für Anilin-fabrikation with a supply of the material prepared by the method given in the Schöllkopf patent, the authors took occasion to submit this to examination. They find that it is converted by the hydrazine method into naphthalene-1:4'-disulphonic acid, which was characterised by conversion into the chloride crystallising from benzene in prisms melting at 182°, and into 1:4'-dichloronaphthalene melting at 107°. On treatment by the Sandmeyer process it gave a chlorodisulphonic acid, the chloride of which crystallised from acetic acid in very small prismatic needles which became opaque on drying, and from a mixture of petroleum spirit and benzene in sparingly soluble glistening flat plates; it melted at 135°, and, on distillation with PCl₅, was converted into δ - or 1:4:1'-trichloronaphthalene melting at 131°. These results place it beyond question that the constitution of the Schöllkopf acid is expressed by the formula—



61. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 6. The Constitution of Cassella's β -Naphthylamine- δ -disulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

Messrs. Cassella and Co. having been good enough to furnish the authors with a supply of their β -naphthylamine- δ -disulphonic acid, prepared from the β -naphthol-disulphonic acid of their German patent No. 44079, it has been possible to determine its constitution by the hydrazine and Sandmeyer methods already described. On treatment by the hydrazine method, the amido-acid yields, in the first instance, a peculiar ropy gelatinous hydrazine, which can only be freed from tin salts with considerable difficulty. The disulphonic acid obtained from this hydrazine yields a chloride crystallising from benzene, in which it is sparingly soluble, in small flat spear-like needles; this chloride melts at 225°, and on distillation with PCl₅ yields 2:3'-dichloronaphthalene melting at 135°: it is, therefore, naphthalene-2:3'-disulphonic acid—the β -disulphonic acid of Ebert and Merz. By the Sandmeyer method, the amido acid is converted into a chlorodisulphonic acid, the chloride of which crystallises from benzene, in which it is very soluble, in small characteristic radiate groups of very slender needles, and

from a mixture of petroleum spirit and benzene in small opaque aggregates melting at 176°; on distillation with PCl₅ it yields 2:3:2'-trichloronaphthalene melting at 90°. Combining these results, it follows that Cassella's β -naphthylamine- δ -disulphonic acid and the β -naphthol-disulphonic acid of the German patent No. 44097, from which it is derived, have the formula—



and both are, therefore, tri- β -acids isomeric with the corresponding R-acids (*Proc. Chem. Soc.*, 1890, 12).

62. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 7. The Disulphonic Acids obtained by Sulphonating the Isomeric Heteronuclear β -Naphthylaminedisulphonic Acids." (First Notice). By HENRY E. ARMSTRONG and W. P. WYNNE.

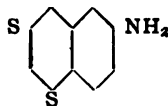
According to Gans and Co.'s German patent, No. 35019, 1884, β -naphthylamine is converted into the amido-G-disulphonic acid by heating its sulphate with thrice its weight of 20–30 per cent anhydrosulphuric acid at 110–140° until soluble in water; and the same product is said to result when " β -naphthylaminedisulphonic acid" is similarly treated. But inasmuch as four monosulphonic acids are obtainable from β -naphthylamine, to determine the law of sulphonation, it was obviously necessary to examine the behaviour of each of these and to avoid the occurrence of secondary changes as far as possible; experiments with this object in view were commenced several years ago: meanwhile an account of the behaviour of the Brönner acid under conditions similar to those specified by Gans and Co. have been published by Forsling (*Berichte*, 1888, 3496).

(1). 2:1'- β -Naphthylamine- α -sulphonic Acid (Badische Acid):—When the Badische acid is stirred into four times its weight of 20 per cent anhydrosulphuric acid at a temperature not exceeding 20°, and the mixture is allowed to stand, sulphonation proceeds slowly and is not entirely complete even at the end of three months. The product is found to consist almost entirely of an acid recognised as amido-G-disulphonic acid, inasmuch as it gave by the hydrazine and Sandmeyer methods all the products already described as characteristic of this acid (*Proc. Chem. Soc.*, 1890, 12). The naphthalenedisulphochloride prepared from it melted at 137°, and on distillation with PCl₅ gave 1:3-dichloronaphthalene melting at 61·5°; the chloronaphthalenedisulphochloride from it melted at 169°, and on distillation with PCl₅ gave 1:3:2'-trichloronaphthalene melting at 113°. The subsidiary product formed on sulphonating the Badische acid has not yet been prepared in sufficient quantity to admit of its examination.

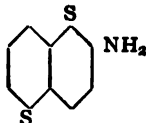
(2). 2:4'- β -Naphthylamine- α -sulphonic Acid (Dahl Acid).—When stirred into four times its weight of 20 per cent anhydrosulphuric acid at a temperature not exceeding 20°, the Dahl acid gradually undergoes further sulphonation, the process being usually completed in 116–120 hours. The product is found to consist of two isomeric acids, which are readily separated by crystallising out the minor product as normal potassium salt, and subsequently purifying the chief product by repeated crystallisation of its acid potassium salt.

Chief Product.—The acid potassium salt of the chief product crystallises in thistle-down like aggregates, and is very soluble in water; on reduction by the hydrazine method it gave naphthalene-1:3-disulphonic acid which was characterised by means of the chloride melting at 137°; on distillation with PCl₅, this gave 1:3-dichloronaphthalene melting at 61·5° (*loc. cit.*). On treatment by the Sandmeyer process, it was converted into a chlorodisulphonic acid, the chloride of which is very soluble in benzene, and crystallised from a mixture of benzene and petroleum spirit in radiate groups of small prisms, from acetic acid in elongated prismatic needles showing good

end faces; this chloride melted at 156°, and on distillation with PCl_5 gave 2:2':4'-trichloronaphthalene crystallising in radiate groups of very slender characteristic needles melting at 80°. It follows, therefore, that the chief product obtained by the further sulphonation of the Dahl acid under the conditions named has the constitution—

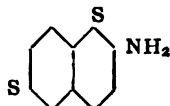


Minor Product.—The normal potassium salt of this acid was obtained in well formed rectangular tablets. The quantity prepared has not sufficed for its complete investigation by both methods, and it has therefore been examined by the Sandmeyer method alone. The corresponding chlorodisulphonic acid yields a *chloride* which crystallises from benzene, in which it is sparingly soluble in the cold, either in prismatic needles or well formed prisms, from a mixture of benzene and petroleum spirit in flat needles, and from acetic acid in long prismatic flat needles; it melts at 158°, and on distillation with PCl_5 is converted into 1:2:4'-trichloronaphthalene crystallising from alcohol in long slender flat needles melting at 78–78.5° (*Proc. Chem. Soc.*, 1889, 49). It follows, therefore, that this amido-acid has the constitution—



(3). 2:3'-β-Naphthylamine-β-sulphonic Acid (Brønner Acid).—When stirred into four times its weight of 20 per cent anhydrosulphuric acid at a temperature not exceeding 20°, the Brønner acid is readily further sulphonated, the process being completed in from 16–20 hours. The product is found to consist of two isomeric acids; the minor product, perhaps 20 per cent, has been identified as G-amidosulphonic acid by the hydrazine and Sandmeyer methods (*o. supra*).

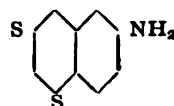
Chief Product.—The acid potassium salt of this acid crystallises in opaque white radiate aggregates of short needles, difficultly soluble in water; but the crystalline form and solubility are much influenced by the presence of small quantities of amido-G-acid, and there is every reason to regard it as identical with the acid obtained by Forsling (*Ber.*, 1888, 3496) by heating Brønner acid with 3 to 4 parts of "fuming sulphuric acid" (percentage of added SO_3 not stated) at 110° until the product was soluble in water. When reduced by the hydrazine process, the amido-acid constituting the chief product gave naphthalene 1:3'-disulphonic acid, which was characterised by means of its sulphochloride melting at 127°, and the derived 1:3'-dichloronaphthalene melting at 48.5°. On treatment by the Sandmeyer process, it was converted into a chlorodisulphonic acid, the *chloride* of which crystallised from benzene, in which it was readily soluble, in well formed prisms, from a mixture of benzene and light petroleum in small prisms showing good faces, and from acetic acid in prismatic needles; it melted at 124.5–125°, and on distillation with PCl_5 gave 1:2:3'-trichloronaphthalene crystallising from alcohol in tufts of short very slender needles melting at 92° (*Proc. Chem. Soc.*, 1889, 52). Combining these results, the amido-acid constituting the chief product, and presumably Forsling's acid, has the constitution—



By operating at higher temperatures the yield of this

acid is diminished, and that of the amido-G-acid increased.

(4). 2:2'-β-Naphthylamine-β-sulphonic Acid (Bayer and Duisberg's Delta-acid).—When stirred into four times its weight of 20 per cent anhydrosulphuric acid at a temperature not exceeding 25°, delta-acid yields a complex product, which has not yet been satisfactorily separated into its constituents. Although the acid was very carefully purified and, it is believed, was freed from Brønner acid, one of the disulphonic acids obtained from it and forming a considerable proportion of the product, had the constitution and properties of the β-naphthylamine-1:3'-disulphonic acid prepared from pure Brønner acid. Two other products were obtained and are at present under investigation; one of these is converted by the Sandmeyer process into a chlorodisulphonic acid which seems to be identical with that derived from the sulphonated Dahl acid of the constitution—

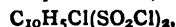


The investigation of the changes which occur in the conversion of these various acids into amido-R-acid on the one hand, and the Cassella β-naphthylamine-δ-sulphonic acid on the other are at present under investigation, and the authors hope to be in a position shortly to communicate in a final form results indicating the influence exercised by NH_2 , as compared with Cl and OH in a β-position on the formation of disulphonic acids.

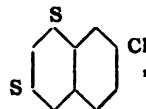
63. "Studies on the Constitution of the Tri-derivatives of Naphthalene. No. 8. β-Chloronaphthalenedisulphonic Acids." (First Notice). By HENRY E. ARMSTRONG and W. P. WYNNE.

As already indicated in a previous communication, the study of the disulphonic acids obtained by sulphonating chloronaphthalenesulphonic acids of known constitution is being carried on *pari passu* with that of the acids derived from the various naphthylaminesulphonic acids (*Proc. Chem. Soc.*, 1890, 18). A brief account of the results obtained with the four heteronuclear β-chloronaphthalenesulphonic acids under like conditions is now given, details with reference to the composition of the salts, &c., being reserved for a full communication. Sulphonation was effected by adding the theoretical quantity of sulphuric anhydride, employed in the form of 20 per cent anhydrosulphuric acid, to the dry potassium β-chloronaphthalenesulphonate and heating the warm mixture at 100° for an hour, the potassium sulphate formed being removed by treatment with alcohol and the excess of sulphuric acid by means of barium carbonate.

(1). 2:1'-β-Chloronaphthalene-α-sulphonic Acid.—This acid, under the conditions named, gives a uniform chloronaphthalenedisulphonic acid, the *chloride*,—



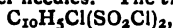
of which crystallises from benzene, in which it is comparatively sparingly soluble, in beautiful radiate groups of long slender lustrous needles; it melts at 170°, and on distillation with PCl_5 gives 1:3:2'-trichloronaphthalene melting at 113°. The constitution of the acid is therefore—



and corresponds with the G-amido acid obtainable from the 2:1'-β-naphthylamine-α-sulphonic acid.

(2). 2:4'-β-Chloronaphthalene-α-sulphonic Acid.—This acid gives what seems to be a uniform product. The potassium salt of the chlorodisulphonic acid is particularly well characterised since it crystallises in prismatic forms,

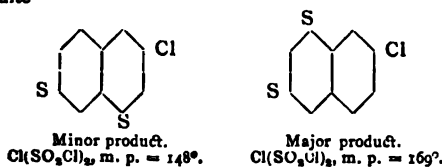
whereas the corresponding salts of the isomeric acids crystallise in slender needles. The chloride,—



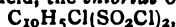
is apparently dimorphous and crystallises from benzene for the most part in very lustrous scales, but occasionally in prismatic forms, both of which melt at $156-156.5^\circ$, and on distillation with PCl_5 give the same trichloronaphthalene melting at 79° . This trichloronaphthalene has not yet been compared by sulphonation, &c., with the 1:2:4'- and the 1:3:3'-trichloronaphthalenes, with one of which it must be identical, owing to the insufficient supply of material; most probably it has the constitution 1:3:3' and corresponds with that derived from the amido-acid constituting the chief product of the further sulphonation of the 2:4'- β -naphthylamine- α -sulphonic acid.

(3). 2:3'- β -Chloronaphthalene- β -sulphonic Acid.—Under the conditions named, this acid gives two chlorodisulphonic acids which are best separated by the fractional crystallisation of the potassium salts. The less soluble potassium salt constituting the minor product yields a chloride, $\text{C}_{10}\text{H}_7\text{Cl}(\text{SO}_2\text{Cl})_2$, which crystallises from benzene in aggregates of what at first sight seemed to be radiate prisms, but under a lens were found to be composed of bundles of very slender needles aggregated in prismatic forms, having a silky lustre; it melts at 148° , and on distillation with PCl_5 gives 1:3:2'-trichloronaphthalene, crystallising from alcohol in characteristic tufts of needles melting at 113° .

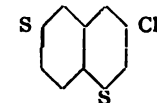
The more soluble potassium salt constituting the major product was found to give products identical with those obtained from the chlorodisulphonic acid derived from 2:1'- β -chloronaphthalene- α -sulphonic acid (*v. supra*). The chloride crystallises from benzene in radiate groups of needles melting at 169° , and on distillation with PCl_5 yields 1:3:2'-trichloronaphthalene melting at 113° . The constitution of the two acids is represented by the formulæ—



(4). 2:2'- β -Chloronaphthalene- β -sulphonic Acid.—This acid, under the above conditions, yields a uniform chlorodisulphonic acid, the chloride of which,—



crystallises in beautiful radiate groups of flat prismatic needles melting at 174° . On distillation with PCl_5 , the chloride is converted into 1:3:3'-trichloronaphthalene, crystallising from alcohol in radiate groups of long slender needles melting at 80.5° . The acid has, therefore, the constitution—



(To be continued).

CORRESPONDENCE.

THE ORIGIN OF MELINITE AND LYDDITE (PICRIC ACID).

To the Editor of the Chemical News.

SIR,—In your issue of the 12th inst. there occurs, page 131, the following sentence:—

"Although picric acid compounds were long since experimented with as explosive agents, it was not until a

very serious accident occurred, in 1887, at some works near Manchester, where the dye had been for some time manufactured, that public attention was directed in England to the powerfully explosive nature of this substance itself."

As this sentence forms part of this year's great annual scientific manifesto, with which Presidents of the British Association for the Advancement of Science are wont to favour your readers, I trust your love of scientific precision will help me to point out that, "*prior*" to the very serious accident near Manchester, public attention "*was*" directed in England to the powerfully explosive nature of this substance itself through the medium of a very serious publication in London—or rather through the medium of two very serious publications—viz., a patent and a paper read before the Chemical Society, as you will see from the following statement, which I drew up last spring at the request of, and as I hoped for the use of, my distinguished fellow-inventor—the President of the Government Committee on Explosives, and now President of the British Association for the Advancement of Science.—I am, &c.

H. SPRENGEL.

54, Denbigh Street, S.W.
May 5th, 1890.

Dear Sir Frederick,—Having had the advantage of Dr. Dupré's friendly advice, I now beg to send you the simple statement, accompanied by all the documentary evidence at my disposal, for which you were good enough to ask in your note of the 29th ult.—Yours very truly and respectfully,

H. SPRENGEL.

Sir F. Abel, C.B., F.R.S., &c.,

President of Government Committee on Explosives.

SIMPLE STATEMENT.

Picric Acid, "*as a powerful Explosive when fired by a detonator*," was discovered and used by me early in 1871. I patented this substance in England in conjunction with a number of other explosive agents.

As this patent (2nd edition) is unfortunately out of print and now older than fourteen years, I am unable to procure and enclose a copy. Be it mentioned, however, that in the complete specification of this patent, No. 2642, of October 5th, 1871, I say, page 5, lines 5 to 8:—

"This invention relates to the preparation and use of explosive compounds, and is partly based on the principle of keeping separate the "*oxydising*" from the "*combustible*" agent until such time as the effect of their chemical combination is required."

Picric acid, being neither an oxidising nor a combustible agent, but partaking of the character of both, already combined, viz., a complete explosive by itself, I separated it from the rest of the substances mentioned in the patent, and placed it alone in a detached sentence, page 6, lines 17 and 18, thus:—"I also employ Picric Acid."

August, 1873, I published a paper in explanation of this patent in the *Journal of the Chemical Society of London*, of which paper I am able to enclose a copy. There I say, page 10 (marked in red):—

"Be it noticed here that picric acid alone contains a sufficient amount of available oxygen to render it, without the help of foreign oxydisers, a powerful explosive, when fired by a detonator. Its explosion is almost unaccompanied by smoke."

(In other words:—It is almost completely gasified by detonation in spite of its excess of carbon, necessitating; as was obvious to every F.C.S., the formation of carbonic oxide. See my table and analysis, pp. 5 and 7.)

A copy of both this patent and paper I sent to M. Eugène Turpin of Paris, February 9th, 1884. Twelve months later this gentleman patented* my statements of 1871 and 1873, respecting Picric Acid, without mentioning the source of his information; and that in spite of the

* Brevet No. 167512 of February 7th, 1885.

sharp reprimand which he had previously received from Sir F. Abel for having brought out, as his own, another invention of mine with much flourish of trumpets. (See my enclosed pamphlet,* pp. 17 to 26.)

Finally it may be recorded, that the first Picric Acid shot was fired by me early in March, 1871, at Faversham in Kent, forming part of a piece of work which want of encouragement and the hostility of gunpowder makers obliged me to put aside.

H. SPRENGEL

London, May 5th, 1890.

ESTIMATION OF AMMONIA.

To the Editor of the Chemical News.

SIR,—I have read a note in the CHEMICAL NEWS of last week, page 126, upon an apparatus for the estimation of ammonia in sewage and sand; the apparatus is also figured.

I should like to draw the attention of your readers to the fact that I employed, while at Bonn, an apparatus almost identical with that described by Mr. Hazen, the only difference being that I used in place of the long, and often inconvenient, Liebig's condenser, a spiral worm of glass, and which I found to answer equally as well. I have occasionally used the method since my return for the determination of ammonia in products obtained from bituminous and petroleum shales, and I cannot say that I have been so favourably impressed with the method as Mr. Hazen appears to be. The method is more complicated, takes up more room, and necessitates the expenditure of more care and considerably more time than the process of simple boiling of the liquid to be examined.

Besides, when using concentrated solutions of ammonia, unless the small flask be continuously heated, my experience has been that it is almost impossible to drive over the last traces of ammonia, thus, of course, yielding results which in most cases are found to be too low. The method, as described is, as Mr. Hazen remarks, useless and inapplicable to water analysis.—I am, &c.,

ARTHUR R. HASLAM, Ph.D.

The Laboratory, Wellington Quay,
Dublin, Sept. 5th, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 9, September 1, 1890.

The Chlorophyllian Assimilation of Trees with Red Foliage.—Henri Jumelle.—In trees with red or copper coloured leaves the chlorophyllian assimilation is always weaker than the assimilation of similar trees with green leaves. The difference of intensity may be very great: the copper-beech, other conditions being alike, assimilates about six times less than the ordinary beech.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 9.

Determination of Acetone in Methyllic Alcohol and the Methylenes of Denaturation.—Leo Vignon.—The crude methyllic spirit used for rendering ethylic alcohols

* "The Hell-Gate Explosion, near New York, and so-called 'Rack-rocks,' with a few words on so-called 'Panclastite,'" by H. Sprengel, London; E. & F. N. Spon, 1886.

undrinkable is known in France as methylene. The author finds that Kraemer's method commonly used may serve for the determination of very small quantities of acetone in methyllic alcohol; it cannot be employed for estimating the acetone in the methylenes used for denaturation, which contain 20 to 25 per cent of acetone. Zieben's method is applicable only to methylenes which contain neither aldehyd nor ethylic alcohol, nor, in general, any substance other than acetone capable of yielding iodoform.

On Oxytetric Acid.—Ch. Cloëz.—The author assigns to this acid the formula $C_5H_6O_4$.

Identity of the Oxytetric and Mesaconic Acids.—Ch. Cloëz.—The result of this paper appears from the title.

The Determination of Hydrochloric Acid in a Solution of Hydroxylamine Hydrochlorate.—J. A. Muller.—This determination can be made with a solution of soda quite free from carbonate, using phenolphthalein as the indicator.

Action of Oxygenated Water on the Oxy-compounds of Manganese.—A. Gorgen.—This memoir does not admit of useful abstraction.

Archives Néerlandaises des Sciences Exactes et Naturelles
Vol. xxiv., Parts 2 and 3.

This issue contains no chemical matter.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Wood Pulp.—Can any correspondent inform us where we can get a detailed account of the manufacture of wood pulp by the most recent process.—R. L. P.

Portland Cement.—Will any correspondent refer me to some reliable books on the manufacture of Portland cement, with special reference to grinding raw material and clinker?—F.I.C.

Foreign University.—What university in Germany or Switzerland is generally considered to give the best training in chemistry, especially with a view to general analysis and agricultural? In other words, which German or Swiss university would you recommend to a man desiring to go abroad in order to acquire a good chemical training, and having in view a general analytical practice, but mainly agricultural?—STUDENT.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1610.

THE RIVER AIRE: A STUDY IN RIVER POLLUTION.*

By T. H. EASTERFIELD and J. MITCHELL WILSON, M.D.

THE following paper endeavours by a series of analyses to show the amount and probable sources of the pollution of the river Aire, from its origin until it reaches the estuary of the Humber. (It had been proposed to treat of the Calder also in this communication; we reserve, however, the results of our investigations upon this river for publication at another time.) In the autumn of 1889 we were engaged in a similar inquiry, but then only with reference to that portion of the Aire which lies at some distance below Leeds, and after it is joined by the river Calder. The facts then ascertained formed the basis of a report to the Goole Local Board by one of the authors of this memoir (J. M. Wilson).

On previous occasions, in dealing with the question of river pollution above Leeds, analyses have been made, chiefly, if not only, of such contributory streams, or becks, as discharge the largest amount of polluting matter into the river. These inquiries doubtless served the purpose of tracing the source of these gross pollutions, but gave little or no idea of the extent to which the whole volume of the river was thereby affected. Our object has been to supply this information.

The points selected by us, in taking samples for analysis, have been chosen with reference to possible pollutions from large centres of population on the banks of the river or of contributing streams, but only at such a distance below the discharge of such pollutions that their average effect upon the river could be properly estimated.

It is notorious that the river Aire has been, and is still being, polluted with every kind of manufacturing refuse and with domestic sewage. A large part of the solid portion of these polluting matters settles in the bed of the river, and there remains during the ordinary flow of the water. The result, however, of a heavy or long-continued rain-fall is to increase enormously the volume of the stream, scouring out the upper parts of the river, and sending the polluting matters nearer the outfall. This action may be a partial one, only affecting a few miles of the river, or it may be so general as to cause a thorough cleansing of the river bed. In each case the deposit on the sides and bed of the river is carried onwards only so far as the force of the current permits; in the one case the solid matter again settles, causing a large increase in the total impurities in the lower parts of the river; in the other case the mass of the impurities is carried to the sea. It therefore follows that the condition of the water at any given point cannot be entirely due to pollutions poured in by any district immediately above that point; rather may we ascribe this condition to local influences, together with impurities originating nearer the source. The coating of the river bed is also broken up through the fermentation of the deposited filth, and the consequent evolution of gas. This action is especially noticeable below Leeds, and is one cause of the offensive odours with respect to which so many complaints have justly arisen. The same cause may also to some extent explain the fact that the amount of suspended solids varies somewhat irregularly in the different analyses.

Since the present paper does not pretend to furnish any-

thing like complete and exhaustive analyses of the samples of water, it became a matter of importance to select which of the impurities present should be estimated in each case. After careful consideration we decided only to have regard to the constituents enumerated upon the wall diagrams, and we believe that the results there presented give a very fair idea of the condition of the river. In all cases we have stated our results in grains per gallon rather than in parts per million, believing that results so stated are much more comprehensible to most Englishmen, and especially to those with whom the metric system is not in daily use.

In any investigation of river pollution it is necessary to bear in mind the state of the river at the time when the research was being carried out; since the impurities in the water vary greatly in quality and quantity, according as the season is wet or dry; while, further, the physiography of the river basin must, at the same time be considered; for, clearly, constituents, which in one case are to be regarded as results of concomitants to pollution, may in other cases be natural to the water, and be no sign whatever of contamination from artificial sources.

In connection with the latter consideration, we venture to submit to you a concise account of the geology of the river basin. Malham Tarn itself rests upon Cambrian states, but the surrounding fells, from which it no doubt receives its chief supplies of water, consist of Yoredale shales, capped by millstone grit. After leaving the town, the river flows about one mile underground through carboniferous limestone, until it emerges at Malham Cove. It then passes still over carboniferous limestone for about another two miles, when it reaches the outcrop of the Yoredale shales, through which it runs until it reaches Skipton. From this point the river directs its course over millstone grit, succeeded by coal measures, until at Castleford it is joined by the Calder, and is now some sixty miles from its source. Here it enters the magnesian limestone district, through which it makes its way for about five miles, then descends for about sixteen miles over new red sandstone, after which it reaches the warpland, where it falls into the Ouse. It will be noticed that the samples of water, of which the analyses are given, were collected on two separate days, August 5th and 20th. The reason for allowing so long a time to elapse between the collection of samples was that, during a portion of this interval, the river was considerably swollen by heavy rains, and it would have served no useful purpose to present analyses of the river when in such an abnormal condition. The first effect of a flood is, no doubt, to bring down an increased quantity of filth, but after the waters have subsided the river is found to be purged from a good deal of its former impurity; hence, in the second series of analyses, the water immediately below Shipley was found to be upon the whole far less objectionable than in the first series, though some of the constituents have remained constant. This is most graphically shown in the series of curves presented to you. Upon these curves the impurities are quantitatively represented by the ordinates, while the abscissæ show the distance from the source of the river at which each sample was taken.

As there is always a certain amount of difficulty in deciding which is the actual source of a river, we have considered Malham Cove as the river head, because here the river first emerges in considerable volume from the foot of the rocks, is easily accessible, and is of such a state of purity that it forms a very convenient standard of comparison. It is true that, even here, the amount of dissolved solids and albumenoid ammonia is considerable but this is not to be wondered at when we consider that the water has originally flowed from peaty fells, and then found its way through and over limestone rocks for a very considerable time before its emergence at Malham. Though the amount of suspended matter in this water was too small for estimation, the colour of the water was distinctly brown when seen even in small bulk, as is so often the case with waters derived from peaty and moorland

* Read before the British Association for the Advancement of Science, Leeds Meeting, 1890, Section B.

Results of Analysis.

	Date.	Suspended solids.	Dissolved solids.	Chlorine.	Free ammonia.	Organic ammonia.	Oxygen required.	Sulphuric acid.
Malham Cove	August 18.	0'0	15'5	0'45	0'0	0'0066	3'6	0'4
Gargrave	" 5.	1'0	17'5	0'7	0'0196	0'0154	1'6	1'8
Skipton	" 5.	1'5	17'5	0'875	0'035	0'0182	2'4	3'1
Above Keighley	" 5.	1'0	17	0'9	0'021	0'014	2'1	2'4
Below	" 5.	2'0	17	1'1	0'0227	0'0192	2'2	2'7
Saltaire	" 5.	1'5	17'5	1'0	0'028	0'0175	1'8	3'1
Shipley	" 5.	7'5	27	1'8	0'0997	0'0455	6'8	5'25
Shipley	August 20.	2'0	21	1'2	0'0297	0'04375	4'45	5'25
Kirkstall	" 20.	2'1	25	1'7	0'1295	0'0595	5'5	5'88
Knostrop	" 20.	6'5	30'5	2'9	0'3535	0'084	5'9	8'73
Allerton	" 20.	4'0	31'5	3'4	0'2905	0'0612	4'9	9'99
Aire and Calder	" 20.	7'5	25'5	3'7	0'231	0'0472	4'1	6'59
River Ouse	" 20.	6'4	17	1'2	0'0875	0'0245	3'0	4'4

sources. This accounts for the enormous reducing power of the Malham water upon permanganate, the water having been collected at a later date than the other samples, when the stream was swollen with brown peaty water from the fells.

Coming now to the consideration of the individual results as recorded in the curves and diagrams, we notice that, in the case of all the impurities, a gradual rise takes place until Skipton is reached, but that a slight fall takes place in the water taken from immediately above Keighley. This is easily explained by the fact that the Aire between Skipton and Keighley receives a considerable volume of clean soft water from the millstone grit. At Keighley the Worth Beck, itself a foul stream, discharges its contents into the river, bringing down a large quantity of trade sewage, and one is surprised that its influence upon the river is so slight. At Saltaire Park the water is nearly of the same quality as at Keighley, but in nearly all impurities there is a slight reduction. One and a half miles lower, however, the river has received the effect of the Saltaire, Shipley, and Bradford districts, and it is here that for the first time the river assumes that objectionable aspect and foul smell which has made the name of the Aire a bye-word in the districts through which it passes. At Shipley the first series of analyses ends. In respect of most of the foreign constituents the second sample is decidedly better than the first; but the difference in the case of the albumenoid ammonia is but small, whilst the sulphates have remained constant. The river was about two inches higher on this occasion than upon the first, but was considerably lower than it had been five days previously. In every case there is a marked increase in the impurities between Shipley and Kirkstall; but from Kirkstall to half a mile below the Leeds Sewage Works at Knostrop, the rise in every constituent is found to be excessive, and in nearly every case the impurities are here found to be at a maximum. This result is of importance, and scarcely confirms a recent statement, "that the river is very much purer when it leaves Leeds than when it enters it." At Allerton the sulphuric acid is at its highest, while the suspended solids are abnormally low. Below the junction of the Aire and Calder the suspended solids have again risen, and a small increase has taken place in the chlorides. Thus, it will be noticed that with the exception of suspended solids, chlorine, and sulphates, the maximum point is just below Leeds; the rise in chlorine and sulphates after passing Leeds is, we believe, chiefly due to chemical works on the river bank, and to a foul beck entering the river at Methley. The abnormal fall in the suspended matters at Allerton is to us inexplicable, for the sample was taken by one of us; we have, however, no reason to doubt the results of our analyses. It cannot be expected that the curves should follow one another with rhythmic constancy. Indeed, if it were so, this paper would be superfluous.

The figures given under the head of suspended solids will, we think, emphatically support the generally accepted

view that the warp—or what may be termed the only non-objectionable foreign ingredient in the river—is not the result of fluvial denudation, but has its origin in marine action on the Yorkshire coast north of the Humber, whence it is carried into the Ouse and Humber by the tide. The largest amount of suspended solids in the river, before it was influenced by tidal action, was 7'5 grains per gallon, and other analyses have shown that other Yorkshire rivers do exceed this, while in the Ouse, near Goole, there were 64 grains per gallon of suspended matter at low tide, and in the same river in October, 1889, during a "fresh" and at flood tide, the suspended matter equalled 263 grains per gallon. Comparing now the Leeds and Bradford areas, we may say that upon August 5th the water after leaving Shipley contained—

5 times as much	suspended matter
1½ "	" dissolved solids
1½ "	" chlorides
3½ "	" free ammonia
2½ "	" organic ammonia
1½ "	" sulphates

as when the water passed from Saltaire Park into the Shipley and Bradford district. In the case of Leeds, the water below Knostrop sewage outlet on August 20th contained—

1½ times as much	dissolved matter
3 "	" suspended matter
1½ "	" chlorine
2½ "	" free ammonia
1½ "	" organic ammonia
1½ "	" sulphuric acid

as in the case of the same water at Kirkstall Abbey. We do not, however, feel able to act as judges in the case of Leeds *versus* Bradford. Our facts show that both districts are responsible for excessive pollution.

Our results may be summed up as follows:—(1) That the river, originally a limpid stream, receives pollution from all the townships on its banks until it passes Leeds, when the pollution has become so great that the effect of smaller towns below it becomes appreciable; (2) that between each centre of population the river appears to cleanse itself to a small extent by natural causes; (3) that nearly all the impurities rise and fall simultaneously, but not in the same proportion; (4) that there is no evidence that the "warp" is chiefly brought down by the rivers, but rather that it is brought up the river by the tide.

If we consider all the results of our inquiry from a practical aspect, it will be admitted that the provisions of the Pollution of Rivers Act, have not been, and are not being, much enforced in the water-shed of the Aire. Each gallon of the filtered water taken throughout the whole length of the river has been shown to contain mineral and organic impurities in ever-increasing amounts. Even the comparatively minute masses of the impurities, which we have shown to be present in each gallon of water

analysed, must, if measured by the daily flow of many thousand gallons of river water, represent enormous quantities of waste material, which might perhaps be more profitably utilised, or serve some other end than that of converting the natural blessing of a pure stream into the doubtful advantage of a navigable sewer.

DETECTION OF IODINE IN THE PRESENCE OF CHLORINE.

(ADDITIONAL NOTE).

By ALEX. JOHNSTONE.

AFTER the iodine has been liberated, as described in my previous note (see CHEMICAL NEWS, vol. lxii., p. 153), by the action of strong H_2SO_4 , the minutest trace of its free presence can be made self-evident by at once pouring into the tube a drop or two of CS_2 , when the well-known characteristic change to pink in the colour of the latter will result from its absorption of the iodine.

Edinburgh University.

THE DRY ASSAY OF TIN ORES.*

PART I.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Concluded from p. 159).

(8). THE effect of potassium carbonate on the cyanide assay was tested by fusing in a naked crucible 5 grms. of ore with 30 grms. of potassium cyanide, to which had been added different quantities of this flux. One-third of the flux mixture was rammed into the bottom of the crucible, and the rest mixed with the ore, except a small quantity kept to be used as a cover. The average time required to complete the assay was ten minutes from the time the charge began to fuse.

TABLE XIV.

No. of Assay.	Charge.				Resulting tin.	
	Ore.	KCy.	K_2CO_3 .	P.c. in mixt.		
	Grms.	Grms.	Grms.	P.c. in mixt.	Grms.	Per cent.
62.	5	30	3	9.09	3.325	66.50
63.	5	30	6	16.66	3.300	66.00
64.	5	30	9	23.07	3.275	65.50
65.	5	30	12	28.57	3.263	65.26
66.	5	30	15	33.33	3.235	64.70
67.	5	30	18	37.50	3.230	64.60
68.	5	30	21	41.17	3.190	63.80

The charges behaved during the fusion just as if pure cyanide had been used. The crucibles remained uncorroded. On breaking, it was found that with the increase of potash in the mixture the crucible was less soaked with cyanide; in the last assay, with 41.17 per cent potassium carbonate, the bottom was blackened only to the depth of $\frac{1}{4}$ inch. The top of the slag was, in all the assays, as smooth as with pure cyanide. The colour had, however, changed; with small quantities of potash, the slag, on the surface as well as on the fracture, had a bluish tinge, which grew deeper, until, in the last assay, it became of a decided blue-grey colour. The structure of the slag became more and more granular, until it was so coarse as to have the appearance of granulated sugar cemented together. Finally, with the increase of potash the lustre of the slag decreased, while at the same time

it grew harder and tougher. The buttons of tin obtained did not differ in appearance from those with pure cyanide.

In Table XIV. two points are striking: first, that the amount of tin obtained grows smaller with the increase of potassium carbonate; and, secondly, that no tin is recovered in the slags or in the crucible. Both facts are probably due to the same cause,* namely, that metallic tin decomposes alkali carbonates, forming stannates which are not readily fusible. In fact, Berthier† says: "By fusing one part of metallic tin with four or five parts of potassium carbonate, a substance is obtained which is liquid, compact, opaque, yellow like wax, and crystalline." In the assays given in the table, the quantity of flux was increased in proportion to the percentage of potash added. As this alone might have had a bad effect on the result, a number of assays were made in which the percentage of potash was the same as in Nos. 64 to 68, the total amount of flux, however, not exceeding 30 grms. They were all very unsatisfactory. Over fifteen minutes were required for the fusion, and there was no regularity in the results. To counteract this, assays were made, to which charcoal had been added to strengthen somewhat the weakened action of the diluted fluxes, placing, however, fluxes free from charcoal in the bottom of the crucibles. The buttons gave higher results, but the irregularity in their weights was the same as before. It would appear, therefore, that the potassium cyanide needs to be practically free from potassium carbonate; 9.09 per cent of the latter showing already a loss of 1.34 per cent in the result obtained.

(9). The effect of sodium carbonate was tried in the same way. Although this alkali is not common with potassium cyanide, it was thought advisable to test it, as, when potassium cyanide is used in blowpipe experiments, it is generally mixed with an equal weight of sodium carbonate.

The mixtures were not so readily fusible as the corresponding potassium charges, and required fifteen minutes, instead of ten as before. They were, however, just as thin when once melted. When cold, the slags were similar to the potassium slags, only more vitreous and harder. The bluish grey shades of colour were missing; the slags were white, but had no lustre whatever; the buttons were, on the whole, the same as above, but showed bead-like excrescences.

TABLE XV.

No. of Assay.	Charge.				Resulting tin.	
	Ore.	KCy.	Na_2CO_3 .	P.c. in mixt.		
	Grms.	Grms.	Grms.	P.c. in mixt.	Grms.	Per cent.
69.	5	30	3	9.09	3.315	66.30
70.	5	30	6	16.66	3.280	65.60
71.	5	30	9	23.07	3.270	65.40
72.	5	30	12	28.57	3.110	62.20
73.	5	30	15	33.33	3.055	61.10
74.	5	30	18	37.50	3.025	60.50
75.	5	30	21	41.17	2.910	58.20

Table XV., it will be seen, contains no columns for tin in slags or crucible, and the percentage of tin extracted is smaller than with the potassium salt, the inevitable

TABLE XVI.

No. of Assay.	Charge.				Resulting tin.	
	Ore.	KCy.	K_2SO_4 .	P.c. in mixt.		
	Grms.	Grms.	Grms.	P.c. in mixt.	Grms.	Per cent.
76.	5	30	0.3	0.99	3.185	63.70
77.	5	30	0.6	1.96	No button	No button
78.	5	30	1.0	3.22	3.060	61.20
79.	5	30	2.0	6.25	2.525	50.50
80.	5	30	3.0	9.09	2.490	49.80
81.	5	30	4.0	11.76	2.435	48.70
82.	5	30	5.0	14.28	2.250	45.00

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly* Vol. iii., No. 2.

† Berthier, "Traité des Essais," 1847, vol. ii., p. 459.
‡ *Op. cit.*, vol. i., p. 445.

TABLE XVII.

No. of assay.	Granular purified. Resulting tin.		No. of assay.	Pure for gold platers. Resulting tin.		No. of assay.	Common fused. Resulting tin.		No. of assay.	Common for mining purposes. Resulting tin.	
	Grms.	Per cent.		Grms.	Per cent.		Grms.	Per cent.		Grms.	Per cent.
83.	3'225	64'50	86.	3'370	67'40	89.	3'220	64'40	92.	3'115	62'30
84.	3'225	64'50	87.	3'355	67'10	90.	2'990	59'80	93.	3'010	60'20
85.	3'100	62'00	88.	3'340	66'80	91.	2'905	58'10	94.	2'900	58'00
Average 3'183		63'66	Average 3'355		67'10	Average 3'038		60'76	Average 3'008		60'16

conclusion being that an admixture of soda has a still more deleterious effect on the result than one of potash.

(10). The influence of potassium sulphate is a very bad one. Bloxam* states that, in the presence of potassium sulphate, stannous and stannic sulphides are formed; the former if the proportion of sulphate be small, the latter if sufficiently large, the stannous sulphide remaining undissolved as a black powder if the slag be treated with water, the stannic sulphide going into solution, and being precipitated as yellow sulphide upon acidulating.

In the experiments, different amounts of potassium sulphate were added to 30 grms. of potassium cyanide, and two-thirds of the new flux mixed with the ore, one-third being placed in the bottom of the naked crucible. The time required for tranquil fusion was ten minutes.

The charges fused readily, and the crucibles were not attacked; the surface of all the slags was smooth, the colour deepening with the percentage of potassium sulphate from light red, with a dark rim, to black. The fracture was at first similar to that of pure cyanide, and grew finer until it became stony; the colour, at first very light peach blossom, became darker, till it reached, with the last assay, a dark flesh-colour. The hardness and toughness of the slags also increased with the percentage of potassium sulphate.

The results obtained show a gradual decrease in the percentage of tin. One per cent of potassium sulphate causes already a loss of 4'14 per cent tin. In assay No. 76 some stannous sulphide was present; it decreased in No. 77, and was absent in No. 78, which, when acidulated, gave a copious precipitate of stannic sulphide. The deleterious influence of potassium sulphate, which was first shown by Bloxam, is thus verified by a series of systematic figures.

(11). Various grades of the commercial potassium cyanide were obtained and tested. The grade of the cyanide can be judged from its general appearance, the pure being coarsely crystalline, soft, and snow-white. The lowest grade—"or mining purposes"—is reached when the structure becomes stony, and strongly resists pulverisation; the colour is a decided grey, resulting from finely divided iron.

In each experiment 20 grms. of the special brand of cyanide were mixed with 5 grms. of ore, 5 grms. being reserved for the bottom of the crucible, and 5 grms. for a cover. The average time required for tranquil fusion was ten minutes.

a. "Granular Purified"—86 to 90 per cent KCy, with some KOCy and K_2CO_3 —1'25 dollars per pound.

The upper slag did not have the beautiful crystalline structure nor the strong lustre of the pure cyanide. It was white, but showed a bluish tinge near the top. The average result is 4'18 per cent too low, and the greatest discrepancy between the single results is 2'50 per cent.

b. "Pure for Gold Platers"—92 per cent KCy, 5 per cent KOCy, and 3 per cent other salts—1'25 dollars per pound.

The general characteristics are the same as those of Nos. 83 to 85, but the results are higher and more uniform.

c. "Common Fused"—85 per cent KCy—0'55 dollar per pound.

* *Journal of the Chemical Society, New Series, 1865, vol. iii., p. 97.*

The upper slag has a stony fracture, and is of a dull white colour. The results are very low and very irregular.

d. "Common for Mining Purposes"—65 per cent KCy—0'50 dollar per pound.

The surface of the slag is smooth, has a dark blue colour with grey and yellow streaks passing through it. The fracture is stony, the slag is hard and tough, and is flesh-coloured. The results are as bad as those from Nos. 89 to 91.

It will be seen that, of the different grades, only the brand "Pure for Gold Platers" produces results—0'74 per cent too low—which are sufficiently accurate for every-day purposes. As these brands represent each a certain definite grade of a particular firm, it will be seen that the assayer is obliged to test each separately, making the ordinary chemically pure potassium cyanide—98 per cent KCy and 2 per cent KOCy—his standard.

THE FIXATION OF ATMOSPHERIC NITROGEN.*

PART II.

By A. A. BRENNEMAN, S.B.†

(Concluded from p. 162.)

7. *The Relation of Ammonia to Cyanogen and the Conditions which Determine the Formation of One or the Other.*—The production of ammonia by bringing together at a high temperature carbon, air or nitrogen, steam, and a basic substance has long been known. The history of the subject, although closely related in many respects to the question in hand, has been omitted in this discussion for want of time. It is, however, difficult to separate two questions which deal, in a certain sense, with different phases of the same reaction. If any definite conclusion can be drawn from the results of industrial experiments it is that higher temperatures favour the production of cyanides and lower temperatures, of ammonia, with the addition also that vapour of water in excess is certainly unfavourable to the productions of cyanides but probably favourable to the production of ammonia. It is possible even that, for a temperature sufficiently high, supposing that it could be maintained against the cooling effect involved in the decomposition of water by hot carbon, the proportion of water above or below a given limit might be the condition determining the production of ammonia in one case or cyanides in the other. It is difficult in the present state of our knowledge upon the subject to mention any conditions, other than variation in temperature and variation in quantity of water, which can account for the production at one time of ammonia and at another of cyanides in a furnace using in both cases precisely similar materials. The belief of Berzelius, Wöhler, Bromelius, and others (*ante*), that formation of ammonia was the preliminary stage in the synthesis of cyanides and that water acted as an intermediary, accords with this view. An

* *Journal of the American Chemical Society, vol. xi., Nos. 1-2.*

† The substance of this article was prepared as an appendix to a commercial report, but has not been printed heretofore in any scientific journal.—A. A. B.

excess of water, both by lowering the temperature and by impeding contact of nitrogen and carbon, would retard the formation of cyanides and proportionally increase the ammonia.

The extraordinary permanence of ammonium cyanide, in comparison with other ammonium salts, at high temperatures (*ante*), taken in connection with the fact that ammonia by itself is dissociated at high temperatures, may indicate that at very high temperatures ammonia can resist dissociation only in presence of a more refractory substance, hydrocyanic acid, with which it can combine. Ammonia in contact with coal, at a very high temperature, forms ammonium cyanide (*ante*). This may be taken to mean that ammonia is more unstable in presence of hot carbon at that temperature than when merely heated alone, and that the portion first decomposed forms hydrocyanic acid, which unites at once with a portion of ammonia not yet decomposed (because not yet in contact with carbon), and thus, in forming the stable compound ammonium cyanide, the ammonia is protected from dissociation or chemical decomposition. But if ammonia is decomposed at these temperatures it is unlikely that it can form under the same condition, while it is evident that cyanogen not only can but does form. We are led then to the hypothesis that, other conditions remaining unchanged, temperature is an important, if not the leading condition, which determines the production, respectively, of ammonia or cyanogen.

With respect to water as a determining cause, it may now be said that while an excess of water probably tends more and more to oxidise or otherwise decompose cyanogen* as fast as it is formed at very high temperature its influence would be merely mechanical in retarding the formation of ammonia at a temperature somewhat lower. When the temperature is sufficiently high to enable carbon to decompose water one of the products of decomposition (CO) is without influence upon the formation of ammonia, while the other, hydrogen, is in the nascent state and therefore in the condition most favourable for union with nitrogen irrespective of the presence of carbon. If water were in a state of dissociation due to heat alone, oxygen coming from water could not, under those conditions, act upon ammonia, since it could unite neither with hydrogen or nitrogen. The case may be stated as follows:—

a. Ammonia is not permanent at very high temperature, except in combination with cyanogen, but is permanent at somewhat lower temperatures, still above a red heat. It is not decomposed by water at any temperature, but at certain temperatures its formation will be favoured by the very conditions that make water an unstable compound, i.e., high temperature and presence of carbon.

b. Cyanogen is permanent at very high temperatures with or without presence of ammonia. Cyanides are probably decomposed by water in excess at very high temperatures.

Finally, the presence of water in moderate quantity at certain elevated temperatures may favour the production of cyanides by permitting a certain formation of ammonia, which is then converted into cyanides, the temperature being lower on the whole than that required for the formation of cyanogen without water. Here ammonia clearly acts as an intermediary, but the temperature, being above a certain limit, favours the production of cyanides rather than ammonia as the final product. At a slightly lower temperature—still, however, above the point at which water is decomposed by carbon—ammonia would form in preference to cyanides and in greater quantity; with an excess of steam ammonia would be the sole product. This may suggest the possibility of working a furnace intermittently with changes of temperature for the production in succession of cyanogen and ammonia, or, what is the same in principle, the working of two furnaces in

conjunction, one to produce ammonia and the other to convert this ammonia into cyanides.

8. *The Influence of Other Gases upon the Absorption of Nitrogen by Carbon.*—The influence of carbon monoxide and carbon dioxide cannot be definitely stated. Bramwell expressed a preference for the latter in his cyanogen retorts, along with nitrogen, but it is hard to find any reason in theory for this preference, since the higher oxide of carbon is always reduced to the lower in presence of hot carbon, and must be so changed in the cyanogen furnace. As it is therefore, an oxidising agent, it should in theory be more objectionable than carbon monoxide. It is more probable that foreign gases, provided they have no oxidising character, merely impede the access of nitrogen to carbon and only act mechanically to retard the union of carbon and nitrogen.

It may perhaps be expected that the above theory should also explain why cyanogen is not formed in a coal fire by simple union of carbon and nitrogen. In the first place it has never been definitely settled that it does not. Many authorities (Binks, R. Wagner, Brunquill) have held with greater or less force to the belief that it does, or at least that it may so form under certain conditions. That it does not form readily or abundantly must, however, be conceded. Again, the instability of cyanogen itself may be such, under the conditions of an ordinary fire, that it is decomposed as fast as formed, and its instant fixation by combination may be essential to its formation in appreciable quantities. The effect of fire gases, carbon dioxide or monoxide, sulphur dioxide, &c., upon free cyanogen has never been investigated, although several of the authorities already quoted have, from their own experience in the synthesis of cyanides, indicated a belief in the influence of one or other of these gases upon the process (*ante*).

9. *The Influence of Hydrocarbons in the Preparation of Cyanogen or Ammonia.*—If hydrocarbon gases or vapours of heavy hydrocarbons were brought into a furnace containing the materials for production of cyanides or ammonia, namely, hot coal, nitrogen, water in greater or less quantity, and an alkali or other basic substance, the result would be a partial decomposition or dissociation in which carbon and hydrogen would be set free, and fixed gases having the composition of the lower paraffines or olefines would remain. Heavy hydrocarbons, oils like crude petroleum, might be used in part to supply the carbon necessary to the reaction; being in a condition of most minute subdivision as set free from combination, it would be most suitable for rapid combination. It is possible also that hydrogen liberated at the same time and in the nascent state would be better adapted to the synthesis of ammonia than at any other time, and further, this hydrogen would be obtained at less expenditure of heat than hydrogen from decomposition of water by carbon. The condition of a furnace fed with hydrocarbon vapours would resemble to a great extent the smoky gas flames of Levoir and Romily (*ante*), in which ammonium cyanide was produced even without the intervention of a base other than ammonia.

10. *The Influence of Pressure.*—The data derived from experiment on the large scale give little information upon this point. Newton remarks (*ante*) that the production of cyanides is improved by a certain pressure and by friction between the solids and gases of the furnace, but this remark applies to very low pressures such as depend merely upon friction in retarding the gases as they are drawn or forced through the alkalis charcoal by a pump. There is no evidence of systematic use of high pressures, exceeding one atmosphere for example, and the furnaces thus far designed for making cyanides or ammonia are none of them adapted to the use of pressure. It is possible that the necessary reaction would be much assisted by pressure. There is every analogy indeed to favour this view. Combustion in compressed air or oxygen is more rapid than at normal pressure; and the union of nitrogen and carbon should be also accelerated. More of the

* Karmrod found that steam passed over hot potassium cyanide caused evolution of ammonia and the heated residue no longer contained cyanogen.

unlike particles are brought in contact in a given time, and the opportunities for combination being multiplied combination should occur in the same proportion. Moreover the heat lost in expansion of gases is lessened and the temperature within the furnace should be more readily maintained.

If it were possible to maintain a pressure of several atmospheres within a furnace while the gaseous contents of the furnace were continually supplied and discharged, there is every reason to believe that the furnace would be more economical and more effective in the production of cyanides or ammonia.

Summary.

The present aspect of the question may be summarised as follows:—

The manufacture of cyanides and ammonia from the nitrogen of the air, while quite possible on the small scale, is beset with difficulties in its economical and commercial application, which, up to this time, have been insurmountable. These difficulties are probably matters relating mainly to construction and to endurance of materials.

At the same time there is still much uncertainty in regard to the chemical and physical conditions most favourable to the fixation of nitrogen.

The following conclusions are the result of the foregoing inquiry:—

1. The temperature necessary for formation of cyanogen may be lower than at first supposed, but certainly not below a high red heat. For ammonia a low red heat is sufficient.

2. The presence of free oxygen is deleterious in all cases.

3. Water in very small quantities is not prejudicial to production of cyanogen, and an excess is probably necessary in the synthesis of ammonia.

4. The long-continued contact of carbon and nitrogen is of less importance than thorough commingling of all reacting materials.

5. The presence of a strong base is essential, but under certain conditions ammonia, produced synthetically, may serve the purpose of a base and effect the synthesis of ammonium cyanide.

6. Alkaline bases are preferable, potash especially, and because of the intermediate action of metallic potassium which is reduced at a lower temperature than sodium. Baryta is the best of the alkaline earths for the purpose.

7. Ammonia and cyanogen are probably formed under conditions differing in respect to temperature and moisture, but otherwise similar, as already indicated. (2.)

8. The presence of carbonic oxide and of reducing gases in general is probably favourable, while oxygen, carbonic acid, and steam in excess (the latter only in the case of cyanogen) are probably injurious. Nothing is known as to the influence of sulphurous acid or hydrogen sulphide, but they are probably undesirable.

9. The presence of hydrocarbon vapours is favourable, and may, under certain conditions, permit the formation of both cyanogen and ammonia without the presence of a base.

10. There are no direct data for estimating the influence of pressure upon the reactions in question. The application of pressure is at least worthy of trial.

Discussion.

Dr. WALLER said that the so-called "catalytic action" afforded no explanation of the effect of certain elements in the cyanogen forming process, and mentioned the apparent inducements offered for the production of a salt by the presence of a base, as, for instance, the formation of calcium chromate by heating chrome iron ore with lime.

Dr. ALSBERG called attention to the fact that addition of lime would in some cases contribute merely physical conditions which would aid in the reaction, such as porosity, infusibility, &c. Also that frequently in such

instances of so-called catalytic action the temperature of formation and of dissociation of the new compound are so nearly the same that unless a base is present to unite with and retain it, as a salt not dissociated at that temperature, no reaction results. He expressed it as his opinion that not even a momentary formation of such compounds takes place under such temperature conditions unless in the presence of a base to retain them. The addition of iron in the cyanogen process has something to do with its success—as in the Castner sodium process.

Dr. DOREMUS referred to the production of oxygen from KClO_3 and MnO_2 , and to a paper published in the CHEMICAL NEWS intended to show the existence of a number of definite successive reactions between these substances. Experiments made with indifferent substances—*e.g.*, sand—substituted for MnO_2 , gave dissimilar results.

Mr. SABIN—The escape of nitrogen as ammonia in the old prussiate process may be very great if the management is unskilful. A cyanide is first formed, and then, at a higher temperature or on prolonged heating, ammonia is produced. I believe that in a properly constructed and continuously acting furnace all of the nitrogen of leather scrap could be converted into ammonia in presence of caustic soda and moisture, although the process might not be economical. I doubt whether any cyanide manufacturers in this country, with one exception, are making a paying business of it, as such large quantities of cyanides and ferrocyanides are imported. The exception, a firm in Newark, are using an improved pear-shaped retort heated only at the central wide portion.

Dr. ALSBERG—We are on the eve of a complete revolution in prussiate processes; cyanides and ferrocyanides are manufactured in Germany from gas purifier waste in such quantities as to have reduced the price 25 per cent. The process of making cyanides from sulphocyanides is not easy because of difficulty of eliminating sulphur. The only practical process at present is by heating sulphocyanides and finely divided iron under pressure at 120–140° C., whereby ferrocyanide and ferrous sulphide are formed. It is also stated that if a sulphocyanide and ferrous sulphate are mixed and exposed to air, that sulphur is gradually taken up in presence of free alkali, but it seems somewhat doubtful. The old method of making cyanides will have to be abandoned for cheaper methods. Sodium ferrocyanide is now made in large quantities to replace potassium ferrocyanide using gas house wastes and commercial soda-ash. More of sodium bichromate is used in dyeing and calico printing than of potassium bichromate, but certain colours, it is claimed, will not permit of this substitution.

Dr. DOREMUS said the Wilkinson process for manufacturing wood gas produced little cyanogen and no ammonia; in fact he had never heard of either as impurities requiring any attention.

Prof. BRENNEMAN—The formation of ammonia by an ordinary coal fire may not be impossible. In the gas retort the amount of ammonia and cyanides produced is very large, possibly larger than that due to the nitrogen in the coal alone, although the access of atmospheric nitrogen, through leakage and attime of charging, cannot be very free.

NOTE.—In regard to the question of action by presence or predisposing affinity, the case, in its strictest sense, is inconceivable. It involves action for a purpose by inanimate things. Also, the supposition that action of a certain kind cannot take place, even momentarily, under conditions in which decomposition also occurs, is a necessity only in theory. It presupposes that every newly formed molecule is instantly solicited by all of the conditions, chemical and physical, that affect the mass, whereas in a reacting mass of solids (less so in the case of liquids or gases, although still existing) there are difficulties in the way of instant diffusion of all conditions. Heat may be locally increased or decreased momentarily by

chemical action, and *vice versa*, and these changes may favour the local formation of products which are instantly fixed by active substances present in excess, and has been already explained (*ante*).—A. A. B.

DETERMINATION OF LITHIA IN MINERAL WATERS.*

By E. WALLER, Ph.D.

PRACTICALLY three methods are now available. (1) The phosphate method (Mayer's modification) (*Ann. Chem. u. Pharm.*, xcvi., 193). (2) The amyl alcohol method (Gooch, *Am. Chem. Jour.*, ix., 33). (3) The fluoride method (Carnot, *Bull. Soc. Chim.* [3], i., 280).

Rammelsberg's method (*Pogg. Ann.*, lxi., 79), somewhat similar in principle to that of Gooch, in that it depends upon the comparatively greater solubility of lithium chloride in an organic solvent, has been comparatively little used, on account of the difficulty and expense involved in obtaining the pure anhydrous alcohol and ether necessary for the process. Moreover the experiments of J. L. Smith (*Am. Jour. Sci.*, [2], xvi., 56), rearranged in convenient form for reference by Gooch (*loc. cit.*), do not indicate that it is very satisfactory in its application, even with the best of care. Some indirect processes, such as the weighing of mixed chlorides of sodium, potassium, and lithium, and then determining the chlorine and potassium (Bunsen, *Ann. Chem. u. Pharm.*, cxxiii., 348), have been also proposed, but they are troublesome in execution and likely to be unsatisfactory in result.

For all of these processes it is necessary to obtain from some known quantity of the water the alkalies as chlorides free from admixture with other bases, and in most cases a considerable proportion of the sodium and potassium salts, which usually predominate largely over those of lithium, must be removed. To accomplish this the usual method may be followed, acidification with hydrochloric acid, evaporation, treatment with barium hydrate solution, removal of the excess of baryta by ammonium carbonate, driving off the ammonium salts, and extraction with alcohol or alcohol and ether to take out the lithium chloride, which is inevitably accompanied by some sodium and potassium chlorides. Throughout this treatment the spectroscopic method must constantly be used to determine when the extraction or washing is complete, and these preliminary operations often prove very tedious. Some suggestions in this connection may be of value. The small platinum wires used to test the precipitates, solutions, &c., need critical examination. A wire which has been once used with lithium salts may perhaps be held in the flame until it will give no trace of colour to the flame, nor show the lithium line by the spectroscopic, but on moistening with hydrochloric acid and inserting in the flame the line will show almost as brightly and distinctly as if no lithium had been removed from it. Repeated scouring, immersion in acid and insertion in the flame, or long soaking in acid may be necessary to remove this trace of lithium from the wires. It has been found convenient to keep several wires dipping into a test-tube partially filled with dilute hydrochloric acid, and to use them in succession, so that each wire shall have a tolerably long immersion in the acid, before being tested again, as a preliminary to using it for a test on a precipitate, &c.

Barium precipitates (BaCO_3 and BaSO_4), when formed in the presence of lithium compounds, carry down and retain perceptible quantities of lithia (by spectroscopic test) with great persistency. The well-known tendency of the barium sulphate to drag other salts with it seems to be greater in the case of lithia than in that of other alkali

line salts, although this may perhaps be due to the exceeding delicacy of the spectroscopic reaction. Precipitation in a rather dilute solution and rather liberal washing is usually the most convenient course to pursue in the case of the precipitation of BaSO_4 in presence of lithium salts. With BaCO_3 a re-solution in HCl and re-precipitation with ammonia and ammonium carbonate is most effective. If the proportion of lithium is large, re-solution and re-precipitation a third time may be advisable. The precipitate produced by barium hydrate, unless consisting largely of sulphate, does not give so much difficulty in the washing out of the lithia, except when it has been exposed for some time to the air of the laboratory containing CO_2 .

A word further as to the decomposition of LiCl by heat. Direct quantitative estimations upon the subject were not made in this investigation, but the phenomena noted tend to confirm Mayer's remark, that under the influence of heat in presence of water, lithium chloride has a tendency to exchange chlorine for oxygen.

A solution containing lithium chloride is evaporated to dryness with difficulty when placed on the water-bath, and if it finally is made to appear dry after prolonged treatment in this manner, more of the material is slow to re-dissolve in water (apparently because of the formation of lithium hydrate) than if the same solution is evaporated nearly to dryness and the moisture driven out by careful ignition over a naked flame.

Assuming in every case that one has obtained a concentrated aqueous solution from a known quantity of the water, containing all of the lithium and some of the potassium and sodium as chlorides, but no other bases, the phosphate method would be as follows:—

Add an excess of hydro-disodium phosphate, and then a moderate excess of pure sodium hydrate, evaporate to dryness, re-dissolve in water by the aid of a gentle heat, add an equal volume of strong ammonia, digest warm for some time, allow to stand for twelve hours, filter, and wash with a mixture of equal volumes of ammonia and water, and finally ignite and weigh as Li_3PO_4 . A second or third portion of precipitate may be recovered by evaporating the filtrate and washings, adding ammonia, and allowing to stand as before, filtering, &c. The chief difficulty with the accuracy of the process consists in the practical impossibility of obtaining all the lithium as phosphate, free from any other alkaline salts. Too much washing will cause appreciable amounts of lithium phosphate to go into solution. Indeed, in my experience the filtrate and washings have always showed a decided lithia line in the spectroscopic from the start. On the other hand, too little washing leaves some alkaline salt along with the lithium phosphate—shown by its tendency to cake on ignition—but whether it cakes or not, lithium phosphate separated by this method, when tested by the flame, almost invariably gives so strong a sodium flame as practically to obscure the red of the lithium to the naked eye. Consequently it becomes to a considerable extent a matter of judgment to decide when the washing is completed, and then the amount of lithium phosphate obtained is a compromise between the precipitate dissolved off by washing and alkaline salts left with it. However, by the aid of a little experience the error can be usually brought within moderate limits, if the proportion of water which the chlorides represent is sufficiently large (ordinarily 10 to 20 litres). The use of such large quantities of water is naturally attended with more or less labour in evaporation, removal of bases, &c., and is in itself objectionable aside from the sources of error inherent in the method of determination. This method has, however, until recently been practically the only one in general use.

The method of Gooch (*loc. cit.*) used by him in the examination of the waters of the Yellowstone Park ("Bull. U.S. Geol. Survey," No. 47; also *CHEM. NEWS*, lix., 113 *et seq.*), may be described as follows:—The concentrated solution of the alkaline chlorides should con-

* *Journal of the American Chemical Society*, xii., No. 6.

tain only about 0.2 grm. of salts in all. To this solution, in a casserole or dish, is added 30 to 50 c.c. of pure *anhydrous* amyl alcohol. The vessel is then heated on a sand-bath over a low flame, so as to boil off the water through the amyl alcohol, leaving the undissolved salts adhering to the sides of the dish. The heat is kept up until the volume of amyl alcohol has been reduced to about 15 or 18 c.c. after cooling. A few drops of hydrochloric acid are added to restore to the form of chloride any lithium oxide or hydrate which may have been formed, and the heating is repeated for a short time. The amyl alcohol is then filtered through paper, or through a Gooch crucible, into a measuring cylinder, and its volume noted (usually 10 to 15 c.c.). In case the proportion of lithium is large the undissolved salts should be taken up with a little water, and the treatment repeated in the same way as just described, the amount of amyl alcohol which has been heated with the chlorides being measured as before. The salts are then washed with cold amyl alcohol until no trace of lithium is perceptible in them by the spectro-scope; the filtrate and washings are evaporated in a weighed platinum dish, and the chlorides converted into sulphates, ignited, and weighed. From this weight, for every 10 c.c. of amyl alcohol which remained in contact with the chlorides after heating, the following deduction is made:—

When only sodium and lithium chlorides were present . . .	0.00050 grm.
When only potassium and lithium chlorides were present . . .	0.00059 "
When both sodium and potassium as well as lithium chlorides were present . . .	0.00109 "

The cold amyl alcohol used for washing dissolves so little that it is needless to take it into account.

The relative solubilities of NaCl, KCl, and LiCl in amyl alcohol, as determined by Gooch, are essentially:—

NaCl	1 in 30,000, or 0.0041 grm. in 100 c.c.
KCl	1 " 24,000, or 0.0051 " 100 "
LiCl	1 " 15, or 6.60 " 100 "

Temperature seems to have but little influence upon the solubility of NaCl and KCl.

Pure amyl alcohol freed from water by boiling, if necessary, is indispensable.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

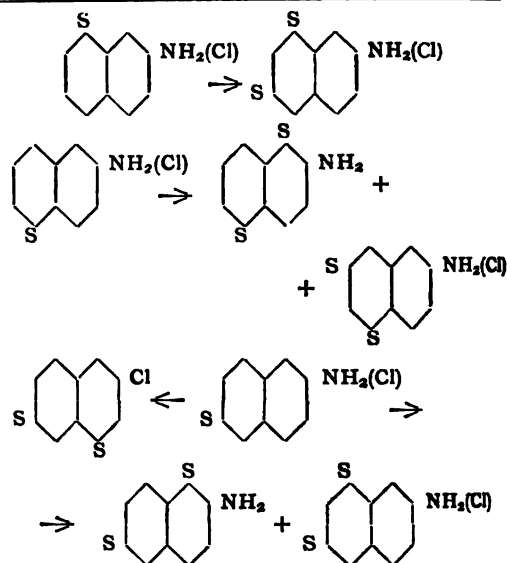
Ordinary Meeting, June 19th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

(Concluded from p. 165).

64. "The Comparative Influence Exercised by the Radicles Cl, OH, and NH₂ in Naphthalene derivatives on the Formation of Disulphonic Acids." By HENRY E. ARMSTRONG and W. P. WYNNE.

The results obtained by the comparative study of the influence exercised by radicles such as Cl, OH, and NH₂ on the formation of disulphonic acids, of which an account has been given in the foregoing notes and in previous communications by the authors, are such as to throw much light on the laws which govern substitution in the naphthalene series, and are moreover highly suggestive. The results obtained in the case of the chloro- and amido-acids are collected in the following diagram:—

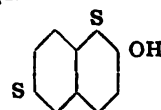


One fact to which attention may be directed, which appears to be most clearly established by the investigation of a very large number of disulphonic acids, is the "invincible objection" of two sulphonic radicles to remain in either contiguous or para- or peri-positions. The expression "remain in" is used advisedly, as the authors believe that, inasmuch as action more often than not takes place in the first instance in accordance with the so-called α -law to which they have repeatedly directed attention, such positions are sometimes initially assumed by two sulphonic groups. It is a question whether the final acquisition of other positions than α -positions is a consequence of direct isomeric change, or of the formation of higher sulphonic acids and their subsequent partial hydrolysis.

Different radicles undoubtedly exercise a very different and most important influence in determining such secondary changes. Thus β -naphthol on treatment with sulphonating agents is converted into a sulphate which very readily undergoes isomeric change into the 2:3'-sulphonic acid; β -naphthylamine sulphate undergoes a similar change, but much less readily, being converted into the 2:3'-sulphonic acid only after long heating at a high temperature: in this latter case the formation of the sulphamic acid probably precedes that of the sulphonic acid, and either the sulphamic acid is formed with difficulty from the sulphate, or, when formed, does not readily undergo isomeric change.

α -Naphthylamine and α -naphthol differ in a similar manner.

When excess of sulphuric acid is used, opportunity is given for sulphonation to pursue a different course: the characteristic properties of the phenol and amine are, in a sense, obliterated owing to the formation of sulphates, and these sulphates behave much as do corresponding derivatives containing a neutral radicle-chlorine, for example. Then, if β -naphthyl sulphate be sulphonated by SO₃HCl without application of heat, a disulphonic acid is at once obtained which, there is reason to believe, has the constitution—



(cf. *Berichte*, 1882, 204); the formation of this compound affords the most significant indication of the course of change: evidently the *homo- α* -hydrogen atom contiguous

to the $\text{O}\cdot\text{SO}_3\text{H}$ -group of the sulphate is first displaced; the resulting sulpho-sulphate, however, spontaneously undergoes isomeric change. β -Naphthylamine sulphate, apparently, behaves somewhat differently, yielding the 2:1'- and 2:4'-monosulphonic acids: in this case the $\text{NH}_2\cdot\text{H}_2\text{SO}_4$ -group may be supposed to remain unchanged; but it is not improbable that the homo- α -hydrogen atom contiguous to this group is primarily displaced by SO_3H , which then passes spontaneously into the contiguous peri- α -position, giving rise to the 2:1'-acid: the formation from the 2:3'- and 2:4'-monosulphonic acids of disulphonic acids containing the SO_3H -group in the homo- α -position contiguous to the NH_2 affords the strongest support to this view. The formation of the 2:4'-monosulphonic acid from β -naphthylamine sulphate is perhaps the outcome of an independent action.

In the case of β -chloronaphthalene, it is conceivable that the 2:1-sulphonic acid is the immediate product, and that this spontaneously changes into the 2:1'-acid which is actually obtained as chief product; the 2:3'-acid which is obtained as subsidiary product may be formed by spontaneous isomeric change from 2:4'-acid initially produced on sulphonation rather than by the isomeric change of the 2:1'-acid at the moment of formation; this view being supported by the fact that β -iodonaphthalene affords a small proportion of 2:4'-acid (cf. *Proc. Chem. Soc.*, 1889, 120).

In short, it is not impossible that the β -mono-derivatives all behave similarly on sulphonation, acting in a minor degree as naphthalene itself would, but chiefly as mono-derivatives: and that the differences in the structure of the ultimate products are due to the different manner in which secondary change takes place under the diverse influences of various β -radicals. The same argument would apply to α -compounds.

The peculiar differences manifest in the case of monosulphonic compounds are also to be noticed in the case of disulphonic (cf. diagram, above)—the product of further sulphonation is, as a rule, simpler in the case of the chloro-acid than in the case of the amido-acid; and change proceeds further in the case of the hydroxy- than in that of the NH_2 -compound, as is evidenced by the formation of R- together with G-disulphohydroxy-acid under conditions which do not give rise to R-amidodisulphonic acid.

In the case of the 2:1'-amidodisulphonic acid, the homo- α -position contiguous to the NH_2 is, perhaps, screened from attack; and either a 1:4-disulphonic acid is first formed, or, under the dehydrating influence of the sulphuric acid present in excess, a *sulphamic-sulphonic* acid is gradually produced, which then undergoes isomeric change: it appears not improbable, from the exceptionally slow manner in which sulphonation takes place, that the latter is the correct explanation. The remaining three isomeric β -amidodisulphonic acids, are in all probability, at an early stage—for it is possible that a sulphamic acid is the first product of sulphonation—if not initially converted into 2:1-homosulpho-derivatives; but it is a question whether these then undergo a simple isomeric change, or whether the final products are formed from them by their conversion into higher sulphonic acids which then suffer hydrolysis. The behaviour of 1:2-chloro- β -naphthylamine on sulphonation (cf. *Proc. Chem. Soc.*, 1889, 36, 48) appears rather to support this latter view, as the passage of the sulpho-group through the positions $1 \rightarrow 2 \rightarrow 3$ takes place with a much greater facility than is usual in cases of non-spontaneous isomeric change. It is true that the conditions under which sulphonation is effected are such that no water is present; but, bearing in mind the tendency of H_2SO_4 to combine with SO_3 , it is by no means improbable that H_2SO_4 itself may effect the hydrolysis.

Lastly, attention may be called to the occurrence of "homo-sulphonation" in the case of the two chloro- β -sulphonic acids; the products in question are, perhaps, direct sulphonation-products, but it is also conceivable

that the 2:1-chloro-sulphonic acid is first formed and that this undergoes isomeric change to the 2:4-acid in consequence of the guarding influence exercised by the hetero- β -sulphonic radical.

The results obtained in the case of the Dahl No. II. acid are of special interest, as one of the sulpho-groups is in the β -position alternative to that occupied in the acid which yields naphthol-yellow S; it is, hence, possible that, in the first instance, naphthionic acid yields a per-disulphonic acid, and not the Schöllkopf acid.

The solution of these various problems will necessitate much further study; but obviously their settlement is of importance in relation to the theory of the formation of substitution-derivatives generally.

65. "Note on the Action of Potash on Naphthalene-1:3-disulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

When the authors' naphthalenemetadisulphonic acid (*Proc. Chem. Soc.*, 1890, 13) is fused with 3—4 times its weight of caustic potash at $280\text{--}300^\circ$ for several hours, it gives a product which consists chiefly of a trihydroxy-naphthalene, $\text{C}_{10}\text{H}_5(\text{OH})_3$ (C = 67.7 per cent, H = 4.6 per cent). This crystallises from water in minute scales, from light petroleum (b. p. = 30°) in small white aggregates of no definite form, and melts at $120\text{--}121^\circ$. It sublimes in lustrous thin scales; is extremely soluble in ether, chloroform, carbon bisulphide, acetone, and benzene; and gives no characteristic colouration with ferric chloride. The study of the action of potash on naphthalenemetadisulphonic acid is being continued.

66. "The Action of Zinc on Dilute Sulphuric Acid." By F. PULLINGER, B.A., B.Sc., late Scholar of Corpus Christi College, Oxford.

The author has carried out a series of experiments with zinc prepared by thrice distilling *in vacuo* zinc purchased as "chemically pure," and has arrived at the following conclusions:—

(i.) That zinc with a perfectly smooth surface is not acted on by dilute sulphuric acid which has been submitted to prolonged boiling.

(ii.) That zinc with a rough surface is readily acted on by acids, but in a less degree by those which have been boiled than by those which have not.

(iii.) That oxidising agents, such as electrolysed sulphuric acid, hydrogen peroxide, and nitric acid, increase the rate of dissolution.

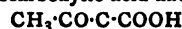
(iv.) That a reducing agent such as hydrogen iodide almost entirely prevents dissolution; but that those containing sulphur, such as sulphur dioxide, are without effect.

(v.) That in all probability persulphuric acid is the *vera causa* of the dissolution of zinc in the so-called "pure" sulphuric acid.

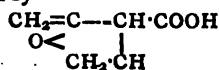
(vi.) That pure dilute sulphuric acid would, at ordinary temperatures, be entirely without action on zinc, whether the surface of the latter were rough or smooth.

67. "Acetyltrimethylenecarboxylic Acid." By T. RHYMER MARSHALL, D.Sc., and W. H. PERKIN, jun., Ph.D., F.R.S.

When ethylene bromide acts on ethylic sodacetacetate, an oil, $\text{C}_8\text{H}_{12}\text{O}_3$, is formed which boils at 196° ; on hydrolysis this yields an oily acid, $\text{C}_6\text{H}_8\text{O}_3$, to which the name Acetyltrimethylenecarboxylic acid and the formula—

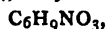


were assigned (*Chem. Soc. Trans.*, 1885, xlvii., 834). In a research published a short time since, Lipp (*Ber.*, xxii., 1201) states, as the results of some experiments on acetopropyl alcohol, that this formula is incorrect, and must be replaced by—



The authors have very carefully re-investigated the subject with the following results:—

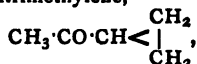
Acetyltrimethylenecarboxylic acid and hydroxylamine readily interact, forming a crystalline hydroxime,—



which melts at 145° . On reduction with sodium amalgam, the acid is converted into α -ethyl- β -hydroxybutyric acid, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{C}_2\text{H}_5)\cdot\text{COOH}$; this forms a thick colourless syrup, yielding on distillation α -ethylcrotonic acid, $\text{CH}_3\cdot\text{CH}:\text{C}(\text{C}_2\text{H}_5)\cdot\text{COOH}$.

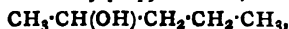
A drop of a solution of potassium permanganate added to a solution of acetyltrimethylenecarboxylic acid in a dilute solution of sodium carbonate is not decolourised, even on long standing—a proof that the acid is a saturated compound, and cannot have the formula ascribed to it by Lipp (compare Baeyer, *Annalen*, ccliv., 146).

Acetyltrimethylenecarboxylic acid readily splits up on heating into acetyltrimethylene,—



and carbon dioxide.

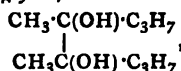
Acetyltrimethylene and hydroxylamine interact to form a hydroxime, $\text{C}_6\text{H}_9\text{NO}$, which crystallises from petroleum spirit in beautiful glittering prisms. When reduced by means of sodium (in moist ethereal solution), acetyltrimethylene yields methylpropylcarbinol,—



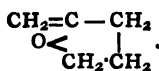
which boils at 119.5° (compare Saytzev, Wagner, *Annalen*, clxxix., 313).

Methylpropylcarbonyl acetate, $\text{CH}_3\cdot\text{CH}(\text{C}_2\text{H}_5\text{O}_2)\cdot\text{C}_2\text{H}_5$, obtained by boiling the alcohol with acetic anhydride, boiled constantly at 133.5° .

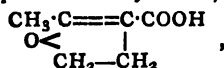
Dimethylidipropylglycol,—



is produced, together with methylpropylcarbinol, by the reduction of acetyltrimethylene. It is a thick oil which boils at 220 – 225° (Friedel, *Jahresb.*, 1869, 513). Fuming solution of hydrogen bromide converts acetyltrimethylene, at ordinary temperatures, quantitatively into acetopropyl bromide, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ (b. p. 120° at 75 m.m.), a proof that acetyltrimethylene cannot have the formula—



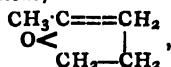
Methyldehydropentonecarboxylic acid,—



is always formed in small quantities, together with acetyltrimethylenecarboxylic acid, by the action of ethylenbromide on ethyl sodacetacetate (Freer and Perkin, *Chem. Soc. Trans.*, 1887, li., 822). In one experiment, this acid was obtained in large quantities and free from acetyltrimethylenecarboxylic acid. It crystallises from benzene in large apparently monoclinic prisms which melt at 150° . It does not interact with hydroxylamine; its alkaline solution decolorises permanganate instantly, in which respects it differs very markedly from acetyltrimethylenecarboxylic acid.

When boiled with water, methyldehydropentonecarboxylic acid is entirely converted into acetopropyl alcohol, carbon dioxide being evolved.

Methyldehydropentone,—



is formed when the acid is distilled. It is a colourless

ethereal liquid; b. p. 82° , rel. den. at $15^\circ = 0.9107$; magnetic rotation, 5.391 . When shaken with water it rapidly dissolves, forming acetopropyl alcohol.

A careful study of these results shows that acetyltrimethylenecarboxylic acid is a saturated ketonic acid, and that it cannot have the constitution proposed by Lipp. Lipp's formula represents an acid which may be identical with methyldehydropentonecarboxylic acid, but which in any case must possess properties closely allied to those observed in this acid, and which are entirely distinct from the properties of acetyltrimethylenecarboxylic acid.

NOTICES OF BOOKS.

The Metallurgy of Steel. By H. MARION HOWE, A.M., S.B. Vol. I. New York: The Scientific Publishing Co.

THE object of the author is to give metallurgists a systematic account of the American steel works and their present practice. In his preface he remarks somewhat dryly that the important thing for the reader is to know that certain practice exists, or is possible; for the manufacturer that it be not known as his particular practice. Probably even the close-mouthed Krupp would object relatively little to having his practice revealed, provided it were not known as his.

The work itself is simply enormous, unmatched in its minute and thorough going comprehensiveness. As a whole it is intelligible only to the rare individuals who are at once thorough chemists and thorough engineers, and who have studied both these disciplines from the point of view of the practical metallurgist. The author, after defining steel—no very easy task—examines the mutual behaviour of carbon and iron, with especial reference to hardening, tempering, and annealing. He discusses at some length the evidence of the state of combination of carbon with iron. It appears that in addition to the graphitic state combined carbon may exist in iron in a more or less soluble modification. He considers, however, that each of these modifications may comprise varieties not as yet distinguished.

In successive chapters the author discusses the behaviour of iron with silicon, manganese, sulphur, phosphorus, chromium, tungsten and copper, and the metals occurring but sparingly in iron. He believes that chrome steel is preferable to carbon steel where extreme hardness is required coupled with a fair degree of forgeableness. Its neglect he ascribes to the fact that its manufacture, which requires unusual skill and intelligence, has largely fallen into careless, incompetent hands.

On the merits of the alloys of iron and aluminium he is sceptical. He notices that some of the most experienced analysts, amongst others Rammelsberg, fail to detect aluminium in wootz, whilst the alloys of iron with larger proportion "appear to be little and hold out little promise." Neither is he satisfied with the evidence of the improvement effected in the Mitis process. He maintains that it is not shown that the melting-point is actually lowered in the Mitis process, that there is reason to doubt if aluminium even tends to produce this specific effect of lowering the melting-point; that were it known to lower the melting-point too little of it is present to explain a fall of the melting-point sufficient to account for the startling effects produced, whilst a fall in the melting-point is incompetent to explain all the phenomena.

An authority quoted has examined many irons and steels for aluminium and finds it commonly present in steel, though in such small proportions as 0.032 p.c. The results of Faraday and Stodart on the alloys of steel with silver, gold, and platinum, have not been confirmed by recent researches nor by practical observations.

Chapters ix., x., xi., and xii. discuss the effects upon

iron of non-metallic bodies, especially in a gaseous or liquid state. Polluted waters corrode iron much more rapidly than clear water. In Thompson's observations while the waste of gas-works does not appear to augment the corrosive action of pond-water initially somewhat polluted by stables, &c., sewage increased it 37 per cent in case of wrought-iron and 76 per cent in case of cast-iron. In these days of iron ships and sewage polluted rivers and harbours the practical meaning of these observations is perfectly plain.

The absorption and escape of gases from iron with the accompanying formation of "blow-holes" and the means for their prevention are very fully discussed. It is considered practically certain that in the cases which have been studied the gases which form blow-holes are chiefly hydrogen and nitrogen escaping from solution; carbonic oxide probably co-operates and doubtless comes in large part from solution. Still air may be drawn down mechanically in "teeming," under conditions which require to be studied, and may thus be an important cause of the blow-holes.

Amongst the methods proposed for the prevention of blow-holes several of the most interesting depend on gaseous pressure applied to the molten steel. Krupp is said to use liquid carbon dioxide at a pressure of 5 tons per square inch. In discussing the value of liquid compression the author writes: "It has seemed to many that Whitworth's attitude has not been one of confidence in the value of his compression." It is admitted, however, that "in proper hands the liquid compression of large masses, if powerful enough, according to our present evidence, does prevent pipes, blow-holes, and cracks almost completely."

The structure of iron as observed on microscopic examination is compared to that of granite. Seven distinct crystalline minerals have been recognised chiefly by the researches of Mr. Sorby. To these the author has given names more brief and of a more mineralogical type than those proposed by Sorby.

Another method of ascertaining the structure of steels is the examination of the fracture, which has been especially studied by Brinnell. This inquirer recognises nine distinct types of fracture which he supposes to result from nine corresponding types of structure. These types of fracture and the conditions under which they are acquired and lost are considered in detail.

The remainder of the volume is devoted to the effects of different kinds of working and to the various processes for conversion.

An appendix describes certain compound steels shown at the Paris Exhibition of 1889.

The Student's Chemistry (Inorganic). In Two Volumes. Poona: The "Orphanage Press."

THE work before us differs from the ordinary small or middle-sized chemical manuals chiefly in two respects; what may be called the philosophy of chemistry has been expounded at greater length, and the physiological action of elements and compounds is brought into prominence. We miss, however, any systematic reference to the spectroscopy and its revelations as well as to electrolysis and to thermo-chemistry.

The arrangement of the work is as follows:—After the introductory discussion of the general principles of the science, in which the bold hope is expressed that before long the synthesis of albumen will have become possible, the author proceeds to a classification of the elements. These he divides into three main classes, non-metals, metalloids, and metals. He is fully aware of the error of applying the term "metalloid," as it is too often done by French chemists, to bodies which are eminently unlike metals. But we fear that by applying it to such elements as tin he will merely increase confusion.

On the addition of alum to impure waters for the purpose of removing organic matter in suspension—it might

have been added "or in solution"—the author thinks the remedy may possibly be worse than the disease, as alum attacks the tissues of the stomach. But the alum, if not added in excess, is decomposed, the precipitate formed carrying down with it most of the microbia which may be present in the water. Since this method has been adopted by the French troops in Tonquin they have enjoyed a nearly complete exemption from dysentery. Facilities for boiling a suspected water are not always at hand.

The use of phosphorus, ordinary or amorphous, for the production of lucifer matches is here rightly objected to. The only legitimate uses of phosphorus, indeed, are in agriculture and medicine.

To the statement that PH_3 in marshy places gives rise to will-o-the-wisp we must demur. The presence of this gas in the air or in the emanations from decomposing animal matter has never been satisfactorily demonstrated.

The author justly objects to the use of boric and salicylic acids for the preservation of articles of food.

Aluminium scarcely receives full justice: the only processes mentioned for its production are those of Deville and Webster, and only one of its alloys is described.

We must congratulate the author on the manner in which he keeps his readers at the level of the most recent discoveries. It is not often in a work of the bulk of the one before us that we find mention of so recent and still questioned a discovery as that of the metal found by Dr. Krüss in commercial nickel and cobalt. We find, too, a notice of the announcement made at the October meeting (1889) of the Vienna Academy of Sciences that sulphur is not a simple body, but a compound of carbon. We must add, however, that this strange result has not hitherto received the necessary verification.

The chief defect of the work is the want of an index, which is the more to be regretted as the arrangement of the book is somewhat complicated.

The second volume is a brief summary of qualitative analysis, and does not call for any special remarks.

CORRESPONDENCE.

M. BARTHE'S NEW SYNTHESSES.

To the Editor of the Chemical News.

SIR,—I am at a loss to understand the following difficulties in M. Barthe's syntheses (CHEM. NEWS, vol. lxii., p. 153):—

Apart from the acetyl constituent, cyanosuccinic ether appears to contain $\text{C}_5\text{H}_6\text{O}_2 + \text{Cy}$ and E_2 ; but cyanosuccinic methers, called methylcyanosuccinate, apparently contains $\text{C}_4\text{H}_3\text{O}_4 + \text{Cy}$ and Me_2 .

In methylcyanotricarballylate, called cyanotricarballylate, what does CA_2 mean?

Information will greatly oblige.—I am, &c.,

S. E. P.

[M. Barthe does not use the expression cyanosuccinic methers. CA_2 is a misprint in the original for CN_2 .]

REFERENCES TO ORIGINAL PAPERS.

To the Editor of the Chemical News.

SIR,—Will you allow me through your columns to make an appeal on behalf of those who have constantly to refer to original papers quoted by authors? The usual method adopted by authors in referring to papers already published is to quote the number of the volume in which the paper or papers occurred; this may seem at first sight to be all that is necessary, and indeed it would be so if everyone had immediate access to a library round whose walls all journals ever published were properly ranged.

I submit, however, that this method renders the ever-

increasing mass of "abstracts" published by the Chemical and other Societies practically useless for reference, and for this reason:—The method gives no clue as to the year in which the paper was published, unless the reader happens to remember what is the number of the current volume of the journal in question, and also how many volumes of it are issued per annum; if he know this, then a few seconds' calculation will enable him to turn to that volume of the "abstracts" published some 4 to 6 months later than the original paper. But as it is impossible for anyone to remember these facts, the absence in the reference of the date of the volume in which the paper occurred makes it exceedingly difficult to find the abstract of that paper.

Inasmuch as it has frequently taken me ten minutes to find the abstract of a paper when only the number of the volume in which it occurred has been given, you will, I feel sure, Sir, make room for this protest against the waste of time suffered by, among others, your obedient servant,

AN ABTRACTOR.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 10, September 8, 1890.

On a Platinum Sulphocarbide.—P. Schutzenberger.—On slowly passing a current of an inert gas, such as dry nitrogen charged with vapours of carbon disulphide, through a column of platinum sponge fixed in a glass tube between two plugs of asbestos, and heated by means of a gas burner to a temperature below dull redness—400° to 450°—the carbon disulphide is entirely absorbed and the platinum sponge is gradually converted, from the entrance-point of the gas to its exit, into a fine black powder. On continuing the experiment as long as there was any increase of weight, exactly 1 mol. of carbon disulphide was absorbed by 2 atoms of platinum. The product had the composition $\text{Pt}_2\text{S}_2\text{C}$. From its behaviour it was found not to be a mixture, but a definite compound, and may be regarded as methane in which the four atoms of hydrogen have been replaced by two bivalent groups, $=\text{Pt}=\text{S}$.

New Researches on the Gadolinia of M. de Marignac.—Lecoq de Boisbaudran.—Last year I had the honour to submit to the Academy the results of a qualitative examination and a quantitative analysis of a gadolinia prepared by M. de Marignac. The results show that nine-tenths of the earth cannot be ascribed to substances previously known. Taking, on the other hand, into consideration the existence of a special electric spectrum, we easily obtain a clear confirmation of the discovery of M. de Marignac, if the researches of this illustrious chemist had not rendered the novelty of gadolinia indisputable. Having been courteously placed by M. de Marignac in full possession of the gadolinia which had served for my above-mentioned experiments, I proceeded to a fractionation of this matter by means of very dilute ammonia. The minuteness of the mass operated upon (1.5 grms.) rendered this research tedious and delicate. In fact, I obtained 14 portions (Nos. -4 to +9); but as the examination of the absorption-spectra requires a certain quantity of concentrated liquid, I was obliged to collect all the matter into the numbers -4, 0, +6, and +9, by the gradual and cautious reduction of the intermediate numbers. In this manner the difference of composition existing between each of these five final numbers and its neighbour (e.g., between numbers 6 and 9) is that which would have been the case if, the earth being more abundant, it had been possible to obtain fourteen portions

of sufficient volume to admit of the examination of each. By absorption, it was found that samarium (characterised by its blue bands) was strongly concentrated in the first precipitates. It is very well marked in No. -4, feeble in No. 6, and scarcely perceptible in No. 9. Thus, samaria shows a basicity less than that of gadolinia. The didymia is naturally concentrated at the tail of the precipitates; it is not perceptible in No. 3, it is very moderate in No. 6, and easily visible in No. 9. By reversal we see that the fluorescence ZB is strongly marked at the head of the series; it is fine in No. -4, moderate in No. 3, doubtful in No. 6, and null in No. 9. Further, the earth No. -4 is very yellow, whilst the earths Nos. 6 and 9 are very pale. The fluorescence of samarium (by reversal) is seen very faintly in No. -4, and not in the other numbers. By the direct spark (not condensed) the spectrum of gadolinium is fine in all the numbers, which is intelligible since the quantity of Gd_2O_3 contained in No. -4, the most impure of all, is still very considerable. In fine, Nos. 6 and 9 contain the smallest quantity of foreign bodies, these consisting principally of Sm, Di, and ZB. There is a little more of Sm but less of Di in No. 6 than in No. 9. I think that the sum of the impurities in each of these two numbers can scarcely reach 2–3 per cent. These are certainly the purest gadolinias which have yet been obtained. No. 6 is a yellowish white; No. 9 is decidedly paler, though not quite white. Professor Clève has kindly permitted me to publish one of the principal results of his long and important researches on gadolinia. He finds that the principal mass is not split up on fractionation. Impurities, very difficult to eliminate, but of known nature, are distributed unequally among the various fractions, altering but little the value of the equivalent, as it will be seen on examining the numbers obtained by M. Clève for the atomic weight of Gd. I will here point out a fact which does not seem to have been noticed; its knowledge will, perhaps, prevent regrettable mistakes among persons who study the rare earths. It is the decidedly great temporary solubility of the rare earths, and especially of gadolinia, in ammonium acetate in presence of an excess of free ammonia. A solution of Gd_2Cl_6 containing from 0.5 to 1 grm. Gd_2O_3 per litre, being mixed, at first with acetic acid and then with an excess of ammonia, remains limpid for a long time, and the precipitation is complete only after the lapse of a day or two days. Heat expedites the formation of the deposit, but in this case it is only partial, since a liquid which has already become spontaneously turbid clears up on heating and becomes turbid when cold. Analogous effects are observed with the salts of Yt, La, and Di. The deposit is formed more slowly with La than with the other two earths. The precipitation is delayed with cerous oxide, but very slightly.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Portland Cement.—If "F.I.C." will communicate with me, I shall be pleased to give him any information I can.—W. J. COOPER, High Street, Mitcheldean.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1611.

NOTES ON OXYGEN.

By J. A. WANKLYN and W. J. COOPER.

Our modification of the Priestley and Cavendish method has given the following results:—

Pure Oxygen Gas.

	Expt. I.	Expt. II.
Oxygen taken	30.0 c.c.	40.0 c.c.
NO added	82.6	97.8
	112.6	137.8
Vol. after reaction ..	20.8	20.0
Therefore contraction..	91.8	117.8
„ oxygen	30.6	39.27

The results obtained on operating on atmospheric air were as follows:—

	I.	II.	III.
Air taken	80.0	50.0	70.0
NO added.. ..	45.0	25.0	54.0
	125.0	75.0	124.0
Vol. after reaction ..	75.6	44.2	80.6
Therefore contraction ..	49.4	30.8	43.4
„ oxygen	16.47	10.27	14.47
Percentage of oxygen ..	20.59	20.54	20.67

We have made experiments on a variety of reagents for the absorption of oxygen. Thus hydrated protoxide of manganese has been tried. This reagent absorbs oxygen from the air, and employing it in a Hempel's absorption pipette, we are able to remove all the oxygen from a specimen of air in the course of twenty-four hours. We do not, however, recommend it for general use.

Alkaline sulphurets, as is well known, were resorted to in years gone by for this purpose. We are using a convenient reagent of this kind made by boiling 18 grms. of sulphur with 24 grms. of caustic potash and 150 c.c. of water. The mixture is boiled in a flask, allowed to cool, and then shaken up with a small volume of air and introduced into the absorption bulbs, a little fresh potash being added. This reagent absorbs oxygen very readily. In about an hour 40 c.c. of pure oxygen may be almost completely absorbed, and very satisfactory results are obtained with air.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

M. CAILLETET showed that the percentage composition of a mixture of two oils could be calculated when we knew the bromine absorptions of the mixture and of its two constituents. The principle of his procedure was this:—A known weight of bromine was added to an oil, and, after digestion, the unabsorbed bromine was estimated. The result was that the higher the bromine-absorption, the smaller was the quantity left free. To render his method clearer, I give his experimental result on a mixture of olive and sesame oils, quoted by Chateau (*Corps Gras Industriels*, Paris, 1864). The solution of turpentine required to decolourise 10 grms. bromine liquor, after digesting with 5 grms. olive oil, is 10.7 grms., and with

sesame oil 4.03 grms., and for a mixture of the two oils is 7 grms.

Difference between 7 and 4.03 = 2.97 } sum of diffs. =
 „ „ 7 and 10.7 = 3.70 } 6.67

$$\frac{10.7 \times 2.97}{6.67} = 4.76 \quad \frac{4.03 \times 3.70}{6.67} = 2.24$$

10.7 : 100 :: 4.76 : 44.53 olive oil
 4.03 : 100 :: 2.24 : 55.47 sesame oil.

100.00

This is simplified by the following proportions:—

$$10.7 - 4.03 : 7 - 4.03 :: 100 : x = 44.53$$

$$10.7 - 4.03 : 10.7 - 7 :: 100 : y = 55.47$$

Writers on oils have recorded the iodine-absorption per cent, which, unfortunately, is not well adapted for these calculations, and considering that the *unabsorbed* iodine has to be estimated to obtain the percentage figures, there is no reason why the results could not be tabulated so as to render Cailletet's method of calculating available. The Hubl figures form an ascending series; whereas Cailletet's process involves a descending series; consequently, if we have two oils to deal with, we have simply to reverse the figures for the iodine-absorption thus: call olive oil 106, and sesame oil 84.5; lard oil 170, and linseed oil 52.5.

I have taken Cailletet's mixture and adapted it to the known and accepted iodine-absorption in accordance with this arrangement. The Hubl being used in the usual way.

106 - 84.5 : 106 - 96.4 :: 100 : 44.65 olive oil
 106 - 84.5 : 96.4 - 84.5 :: 100 : 55.35 sesame oil
 170 - 52.5 : 170 - 84.5 :: 100 : 72.7 lard oil
 170 - 52.5 : 84.5 - 52.5 :: 100 : 27.2 linseed oil.

$$100 \times 96.4 = (100 - x) 84.5 + 106x \quad (1).$$

$$100 \times 96.4 = (100 - y) 106 + 84.5y \quad (2).$$

Solving, &c., $x = 55.35$ sesame oil
 $y = 44.65$ olive „

$$100 \times 84.5 = (100 - x) 52.5 + 170x \quad (3).$$

$$100 \times 84.5 = (100 - y) 170 + 84.5x \quad (4).$$

$x = 27.2$ linseed oil
 $y = 72.8$ lard oil.

Taking the results of (3) and (4):—

$$27.2 \times 170 \text{ (iodine-absorption for linseed oil)} = 4634$$

$$72.8 \times 52.5 \text{ „ „ lard „} = 3822$$

$$\text{Adding and dividing by } 100 \quad \dots = 84.56$$

we obtain the number corresponding to the iodine-absorption of the mixture.

The method of calculating by proportional parts is recognised, and no doubt admits of extensive application in chemical analysis, where a separation is tedious. Thus, a mixture of sodium and potassium chlorides can be arithmetically determined by first chemically fixing on the quantity of Cl and dividing this between Na and K proportionally to their atomic weights (Thorpe's "Inorganic Analysis," art. Indirect Estimation of Na and K). I take the examples given in CHEM. NEWS, vol. lxii., p. 125:—

42.8 iodine-absorption due to olive oil and 53.6 due to sesame oil.

$$\frac{96.4}{42.8} = 2.252 \quad \frac{96.4}{53.6} = 1.798$$

Adding these ratios = 4.05.

$$\frac{2.252 \times 100}{4.05} = 55.6 = \text{sesame for olive.}$$

$$\frac{1.798 \times 100}{4.05} = 44.4 = \text{olive for sesame.}$$

In order to follow the line of reasoning which forms the basis of these calculations, we must bear in mind that the

figure given as the iodine-absorption is really for 100 parts of that oil, and we must not confound the iodine-absorption as the weight of oil required, although, of necessity, it is a measure of the ratio of that oil.

The general result is, that in the case of a mixture of two oils, if we use the Hubl figure or value of absorption, we must reverse the proportion as regards weights, unless we use the equations 1, 2, 3, 4, which are sufficiently self-evident as to require no further explanation. The advantage here is that we can use the Hubl figure as at present understood; and, so far as I can see at present, the figure is independent of the quantity of Hubl reagent used.

ON THE PRESERVATION OF SOLUTION OF SULPHURETTED HYDROGEN.

By A. J. SHILTON, F.C.S.

ON the 15th of November last I published in the *CHEMICAL NEWS* a note on the use of glycerin in preserving sulphuretted hydrogen in solution. The experiments I quoted showed most conclusively that glycerin is most beneficial in this way, and it occurred to me that certain other analogous substances would probably act in a similar manner.

I have made rough qualitative trials, which prove this to be the case.

About five months ago I sealed up bottles containing respectively—

- (a) Sulphuretted hydrogen water.
- (b) " " " with sugar.
- (c) " " " " salicylic acid.

I have opened these to-day, and I find that solution (a) gives no reaction with lead acetate, and is entirely free from odour; whilst solutions (b) and (c) have a strong odour of the gas, and yield copious precipitates with lead acetate. I am at present engaged in further experiments as regards the action of other bodies, not only on sulphuretted hydrogen, but also on other gaseous solutions. The amount of sugar used was 2 per cent, and of salicylic acid 1 per cent.

AN APPARATUS FOR VAPOUR-DENSITY DETERMINATIONS.

By J. A. HARKER,

Research Student in the Owens College, Manchester.

HAVING repeatedly noticed in the laboratory exceedingly cumbersome arrangements for vapour-density determinations according to Victor Meyer's method, I thought it worth while designing a convenient portable form of apparatus for this purpose. The stand consists of an iron rod 1 metre high, screwed into a heavy rectangular iron base about 25 × 17 c.m. near the edge, and in the middle of the longer side. This form of stand gives the greatest stability. Instead of the usual copper cylinder, a small air-bath, similar to those described by Lothar Meyer, serves as the source of heat. A convenient size is 30 c.m. high, having the inner space of 60 m.m. diameter. The pipe of the ring burner is 16 m.m. diameter, and has 20 one-m.m. holes, at a distance of 18 m.m. apart. The air-bath, which is built up of three concentric cylinders, is mounted on an iron plate, having a screw by which it can be clamped on to the stand at any height. This is much more convenient than the usual tripod. The air-bath, when intended for ordinary use, is better without an asbestos jacket. The temperature without a jacket may, with the burner described, be varied from 80° to 360° C., and with a jacket of asbestos $\frac{3}{8}$ in. thick from 140°

to 460°. With the small flames used it is unnecessary to mix the gas with air before burning. No smoking takes place, the gas consumption at the highest temperature being only about 2 feet per hour. For lower temperatures than 80° C. a burner with fewer holes must be used. As a test of constancy the air-bath was lit, and the temperature rose in ten minutes to 201° C. It remained for an hour between this temperature and 202.5° without any screening from draughts, and without either regulator or governor on the gas supply. The rest of the apparatus consists of an iron table, 13 c.m. diameter, fastened to a rod, fitting the boss of an ordinary clamp. This supports a crystallising dish of 12 c.m. diameter and 5 c.m. deep, holding water, in which is immersed the graduated tube for measuring the evolved gas, held by a small clamp. A second clamp holds the vapour-density tube, which should have the capillary limb, on which a small bulb is blown, fastened by indiarubber, and not rigid as usually supplied. The apparatus has been tested by several people and found satisfactory, and the air-bath described has been found useful for many purposes. It may be provided with rings to partially close the hole at the top when necessary. The complete apparatus may be obtained from Mr. E. Hargreaves, Booth Street West, Manchester.

NEW CALEDONIAN NICKEL ORES.

By THOMAS MOORE.

AMONGST the many ore deposits and formations of this island few are probably of greater interest, either from a chemical or commercial point of view, than those of nickel. The nickeliferous ore commonly known as garnierite, is almost invariably found either in, or at least in close proximity to, those huge masses and mountains of serpentine which form a characteristic feature of the place, and are as diversified in their extent as in their richness. With but one or two rare exceptions it is found only on elevated positions, often at the very summits of the mountains, not unusually accompanied by chrome iron ore, and surrounded by a peculiar red earth rich in iron, which by being alternately deluged by the rains and baked by the sun has become hardened together into a compact mass. The nickeliferous mountains present a very bare, sombre, and uninviting appearance; vegetation is extremely sparse and scanty, and the few stunted shrubs growing there seem only to intensify the barrenness of the dull and monotonous region, contrasting strangely with the profuse tropical growth on the lower levels. The colour of the ore varies from the blue-green in the poorer specimens to a warm dark green in the richer, and passing by almost imperceptible shades to a light brown, and, finally, to a fine chocolate colour. The rich ore is generally a mechanical mixture of apparently homogeneous green or brown substance, with rounded pebbles of serpentine, forming a kind of agglomerate, or it is interstitially deposited between thin layers of quartz, steatite, and various hydrated silicates of magnesium.

Miners recognise three varieties of the ore, *i.e.*, quartz rich green, magnesia rich green, and the brown ore. The first is characterised by the large amount of silica it contains, generally as minute glistening crystals of quartz or in the amorphous condition. The magnesia ore contains only a small quantity of quartz, but a very considerable amount of magnesian silicates, and has a paler green colour than the former. The brown ore is the least common variety, is very soft, and as a rule contains only small quantities of quartz and magnesia, but much ferric oxide. Generally speaking, however, they are classified into the green and the brown minerals.

From time to time analyses of the ore have been published, leading to a variety of formulæ with this feature

only in common, that it is a hydrated silicate of nickel, in which the nickel is replaced to a greater or lesser extent by magnesia or oxide of iron. Perhaps the various complicated and somewhat contradictory formulæ devised may be accounted for by the difficulty in obtaining pure pieces, and that the finely intermixed quartz may have escaped observation, thus giving a percentage which does not truly represent the combined silica, but rather that of silica+quartz, for pieces of the ore which to the eye appear thoroughly homogeneous in the great majority of cases give an amount of insoluble silica varying from 2 to 10 per cent. Nevertheless, I have frequently observed that those ores containing much magnesia give differences in analysis which do not agree relatively to any distinct formulæ, but seem rather to indicate a mixture of silicates; as, however, the magnesia diminishes these differences are gradually reduced, and the composition then becomes more constant, and more closely complies with the calculated numbers, except for the combined water, for which I have been unable to find a constant factor. Having excellent opportunities for procuring pure specimens, and from the many hundreds of analyses made of the same, there seems to be no doubt that both kinds of ore approach very nearly to hydrated sesqui-silicates of nickel, giving a formula of $7NiO \cdot 6SiO_2 \cdot xH_2O$, part of the nickel in the green ore being replaced by magnesia, oxide of iron, or alumina, the magnesia predominating, whilst in the brown the oxide of iron is in excess. The following carefully executed analyses of both ores give only the amount of soluble silica, as in those cases when quartz was present it has been calculated out:—

	1.	2.	3.	4.	5.	6.
SiO ₂ ..	35'55	36'24	35'25	34'78	35'80	20'57
NiO ..	48'38	44'94	46'30	43'79	43'54	15'56
MgO ..	5'02	8'75	—	2'75	2'65	0'87
Fe ₂ O ₃ ..	1'41	0'21	0'00	6'30	10'73	49'03
Al ₂ O ₃ ..	1'09	1'03	—	—	—	—
Cr ₂ O ₃ ..	0'15	—	0'14	—	—	3'82
MnO ..	—	—	—	—	0'19	trace
H ₂ O ..	8'85	8'98	9'20	12'40	8'00	10'32
	100'45	100'15	99'89	100'02	100'91	100'17

Nos. 1 and 2 represent the composition of the green ore. The colour is a fine brilliant grass-green. Hardness, 2–3. Specific gravity, 3'00. Streak light green, waxy lustre, and slightly translucent at the thin edges. Before the blowpipe the colour darkens, becoming dark olive green; in presence of much ferric oxide, red.

Nos. 3, 4, 5, and 6 give the composition of different brown ores. The colour varies from light brown to a deep sometimes slightly translucent chocolate; streak yellow or brownish yellow; the fracture is conchoidal, with a very strong resinous lustre. Hardness and specific gravity about the same as the green ore, and rather more brittle. The very light brown species (No. 6) bear a great resemblance to limonite, and are so soft as to be easily marked by the nail. They, however, do not appear to belong to the same class of ores as mentioned above, as the silica fluctuates with the nickel and magnesium oxides, and is sometimes very low, as little as 5 per cent is not unusual. A fact worth noting in connection with oxide of iron deposits is, that although containing oxide of chromium up to 8 per cent, they are easily and entirely soluble in warm dilute hydrochloric acid.

Exposed to the action of the weather all these ores gradually crumble to a powder, the brown exhibiting this to a more marked extent than the green. They are easily dissolved by hot hydrochloric acid, and the silica which separates out does not take the gelatinous condition. Up to the present no trace of crystalline character has been found, although some magnesia-rich specimens occasionally present an appearance similar to asbestos.

Thio, New Caledonia, July 20, 1890.

THE PREPARATION OF BORAX GLASS BY THE ACTION OF BORACIC ACID UPON SODIUM CHLORIDE.

By H. N. WARREN, Research Analyst.

BORACIC acid, as is well known, when in solution is readily replaced by all other acids, but when in a fused condition existing as boric anhydride, an almost exactly reversed action is presented, replacing even to a considerable extent such acids as sulphuric, phosphoric, and others of a similar stability. The action obtained thus by introducing boric anhydride into fused sodium chloride is attended by the slow expulsion of gaseous hydrochloric acid, together with an equivalent of fused borax. This reaction is in every way more productive, however, when boracic acid is introduced in place of the anhydrous compound; and in conducting the experiments a pound of common salt was maintained in the fused condition, while about half its quantity of boracic acid was generally thrown on to its surface. On each fresh addition of acid clouds of HCl were evolved, and a considerable quantity of apparently fused borax was left floating upon the surface of the remaining salt. This after cooling was readily detached from the surrounding salt by breaking the crust, leaving a large fused glassy nucleus absolutely free from sodium chloride, but containing besides borax upwards of 50 per cent of fused boric anhydride. Since apparently the moist acid afforded the best results, the addition of steam was resorted to, and injected during the process of fusion. This undoubtedly raised the percentage of borax to about 80 per cent, still leaving a considerable excess of boric anhydride, and mechanically volatilising a considerable quantity of boracic acid. The remaining experiments, which were carried out more elaborately, consisted mainly in exposing to different grades of temperature mixtures in different proportions of the two compounds, and supplying superheated steam. With these, as in the former, however, too large a quantity of boracic acid, together with the difficulties in regulating the process, have up to the present prevented its practical use.

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DETERMINATION OF LITHIA IN MINERAL WATERS.*

By E. WALLER, Ph.D

(Concluded from p. 174).

GOOCH'S test experiments with mixtures of pure salts may be here quoted, arranged in a form slightly different from that given in his paper. The Li_2SO_4 obtained was calculated back to LiCl in every case. The error is noticeably greater in the presence of potassium chloride.

Ex. pt. No.	Conditions.	LiCl taken.	Errors in corrected weight of LiCl found.
23 ..	NaCl only	Single 0'1298 grm.	0'0002— grm.
24 ..	" "	extr'n 0'1227 "	0'0002— "
32 ..	" "	Double 0'1287 "	0'0007— "
33 ..	" "	extr'n 0'1347 "	0'0006+ "
26 ..	KCl only	Single 0'1256 "	0'0008— "
27 ..	" "	extr'n 0'1287 "	0'0010— "
34 ..	" "	Double 0'1125 "	0'0003+ "
35 ..	" "	extr'n 0'1251 "	0'0011+ "

The average of these errors is 0'0001— with a range from 0'001— to 0'0011+, or if we calculate to the equivalent in $LiHCO_3$ from 0'0016— to 0'00176+, a difference of 0'00376 grm.

* Journal the American Chemical Society, xii., No. 6.

The process has the advantage that the sodium and potassium chlorides are left in a condition for the determination of those bases, in which case, however, an allowance must be made for the small amounts dissolved by the amyl alcohol which was heated with the chlorides. One disadvantage of the process is to be found in the fumes of the amyl alcohol, which, even in a well-ventilated laboratory, is a source of great discomfort to most analysts.

The small amount of water, 100 to 200 c.c., that can be used for this process is advantageous, though for those accustomed to the use of the phosphate process, the amount seems hardly large enough to give a fair average, and to average on a larger amount requires the concentration of the LiCl by extraction with alcohol or alcohol and ether. In some of the first trials made with the process, the amount of mixed chlorides experimented upon considerably exceeded 0.2 grm., probably nearer 1.0 grm., and in some cases more. This was because Prof. Gooch's paper seemed to imply that the operation might be reasonably expected to be successful when applied to quantities ordinarily handled in analytical work. In the case of one water it did prove so, but with another water, containing more lithia as well as alkaline salts, it was not. The removal of all the water in the manner described was a matter of extreme difficulty, and curiously enough, a limit seemed to be reached, beyond which the LiCl was extracted, but slowly and with great difficulty. The results may prove interesting.

The alkaline salts from two equal quantities of a water, each lot amounting to between one and two grms., were treated as described:—

Obtained from A 0.2400 grm. Li_2SO_4 , from B 0.2354 Li_2SO_4 .
Found in insoluble part. f. A 0.0974 " " 0.0943 "

Total .. 0.3374 " " 0.3297 "

The control process used in this case was Carnot's fluoride method, which cannot, however, be regarded as absolutely free from imperfections. It is as follows:—The mixed alkaline chlorides, after evaporation nearly to dryness, are extracted with a mixture of about equal volumes of alcohol (of 90 per cent or over) and ether, so as to obtain the LiCl comparatively free from the others. It was found most convenient to add the alcohol ether mixture, and allow to stand for some time with frequent stirring, and then after standing over night to filter through a small filter and wash with alcohol; one extraction will often suffice. A second extraction may, however, be necessary, the work being of course controlled by the indications of the spectroscope. After evaporating off the alcohol and ether, the salts are dissolved in the least possible quantity of water, and filtered into a weighed platinum dish. The filtrate and washings should then be concentrated to small bulk (5 or 10 c.c.) and pure ammonium fluoride and ammonia added; after thorough mixing, the dish is set aside over night for the LiF to precipitate. The solution is then decanted through a small filter, and the precipitate is washed by decantation three or four times (5 to 7 c.c. at a time) with a solution consisting of the reagent mixed with 5 to 10 times its bulk of ammonia; between decantations the solution must be allowed to stand some little time with stirring. The bulk of filtrate and washing (30 to 50 c.c.) is noted, the filter-paper and contents placed in the dish, sulphuric acid added, and heat applied until the paper has been incinerated, and the lithium converted to sulphate, in which form it is weighed. To this weight is added 0.0040 grm. for every 7 c.c. of filtrate and washings, and the result estimated as Li_2SO_4 is calculated to Li , LiHCO_3 , &c., according to the requirements of the case.

Care is necessary in preparing the reagent and wash liquor.

Carnot seems to have found that the ammonium fluoride ordinarily supplied for laboratory use is the only

member of the combination liable to contain impurities which would interfere (chiefly fluosilicic acid, which might precipitate alkaline fluosilicates), but experiments have shown that ammonia which has been standing for some time in contact with glass will give a cloud (presumably ammonium fluosilicate) with a mixture of solutions of ammonium fluoride and ammonia after boiling and filtering clear. This solution, so long as it contains a fair amount of free ammonia, appears to be without action upon glass. It has been found advisable, therefore, to make up (and cork up) the reagent and washing solution some time beforehand, and to filter off such portions as may be required at the time of using. Naturally, it is necessary to use for the final filtration a filter-paper which has been extracted with hydrofluoric acid. Schleicher and Schull's papers were found satisfactory in this connection. Carnot also recommends that the resulting Li_2SO_4 should be dissolved in 40 to 50 c.c. of water, and a test made for the presence of magnesium, which may have remained with the alkaline chlorides. If any is found to be present, it must be determined as phosphate, and a correction made accordingly.

In connection with this process it was observed that lithium sulphate ignited in contact with the carbon of the filter-paper is especially prone to reduce to sulphide, and especial caution is necessary at this stage of the operation. The sulphide, when heated in contact with the platinum, attacks it in a very marked manner.

The process seems to be very good, although not rapid. Its tendency is to yield results a little high, apparently because the allowance for solubility is usually larger than the actual amounts of precipitate dissolved. Test analysis tended to show also that unless the amounts of potassium and sodium chlorides present with the lithia are kept within narrow limits, the results will be high.

Unfortunately a number of the tests and comparison experiments with these methods have not yet been completed, and will have to be deferred to a second communication.

In order to test these methods upon water containing lithia, samples of several of the best known and widely advertised waters were purchased and submitted to examination.

The results were somewhat surprising, and showed unquestionably that either the original analyses, on the strength of which those waters are now sold, were erroneous on account of imperfection in the methods used, or, what is more probable, that the proportions of lithium in those waters are liable to great fluctuations.

The results given were chiefly obtained by Carnot's fluoride method, but were in several cases confirmed by the use of other methods. The most scrupulous care was exercised to be sure of obtaining *all* of the lithium in the waters under examination, the spectroscopic indications having been used at every stage of the process.

In the Farmville Lithia Water, purchased at the office of the company, no lithium could be detected by the spectroscope on moderate amounts of the water. On evaporating eight litres of the water, and treating in the manner described for the concentration of the lithia into a solution of small bulk, a lithia line was obtained in the spectroscope, but the amount was found to be too small to permit of a quantitative estimation. The experiment was repeated with ten litres of the water, with essentially the same result.

With the Buffalo Lithia Water the reaction for lithium was more distinct, when considerable quantities of the water were concentrated. From twenty litres of the water was obtained lithium sulphate corresponding to 0.0185 part LiHCO_3 per 100,000.

In Londonderry Water the lithia reaction could be obtained without great difficulty. Analysis of the water purchased by myself showed a little over 4 parts per 100,000. The company puts up some of the water in half-gallon bottles not charged with CO_2 , and also some in

Designation of water, &c.	Total solids per 100,000.	Loss on ignition.	Non- volatile.	LiHCO ₃ .			
				Used for determination.	Per 100,000.	Grs. U.S. gal.	Grs. Imp. gal.
Farmville Lithia, half gallon bottles . .	16.4	1.1	15.3	8.0L	trace	trace	trace
" " " " " " " " " " " " " " " "	—	—	—	10.0L	"	"	"
Buffalo Lithia, half gallon bottles . .	93.2	6.5	88.7	20.0L	0.0185	0.011	0.013
" " " " " " " " " " " " " " " "	—	—	—	20.0L	0.0135	0.008	0.009
Londonderry Lithia, half gallon bottles . .	37.35	2.25	35.1	10.0L	4.171	2.432	2.920
" " " " " " " " " " " " " " " "	—	—	—	10.0L	4.075	2.376	2.852
" " " " " " " " " " " " " " " "	—	—	—	2.0L	4.130	2.408	2.891
" " pints (charged CO ₂) .	—	—	—	2.0L	4.129	2.407	2.890
" " " " " " " " " " " " " " " "	—	—	—	4.0L	4.074	2.376	2.851
" " (half gallon, Dr. E.)	5.1	1.0	4.1	1.0L	none	none	none

pint bottles (called in their circulars "sulpho-carbonated"), which is charged with CO_2 , and has also received the addition of some salts. The amounts of salts added appears to somewhat irregular. For instance, the following results were obtained (results given in parts per 100,000):—

	Total	Loss on
	solids.	ignition.
Londonderry, half-gallon bottles (aver.)	37'35	2'25
„ pint bottle, A	149'4	4'9
„ „ B	104'2	4'5
Average of eleven others	224'7	6'4

The variations in the eleven bottles were 221.3 to 231.4 for total solids. The proportion of lithium was essentially the same as for the still water.

I was told that several lots of water, purporting to come from these springs, had at times appeared on the market in which no lithia could be detected. As I learned that Dr. Endemann had obtained some water of that kind, I requested him to send me a bottle. He complied, and although the bottle bore all the labels and marks similar to those purchased by myself, no lithia could be detected in it. The water contained 5.2 parts total solids per 100,000. I have heard of others who had similar experiences.

I naturally desired to obtain samples of these waters direct from the springs, taken by some one whom I knew to be disinterested. Attempts thus far have been unsuccessful. In the case of the Londonderry springs, all access is denied to visitors, and applications for water are referred to the bottling establishment in Nashua.

Of all the waters examined purporting to be natural, the Saratoga Hathorn proved to be the strongest in lithia. The result of tests on this water are not at present in such form that they can be here recorded, but it suffices to say that the water contains fully as much as the analyses call for (12 to 14 parts LiHCO_3 per 100,000, corresponding to 7 or 8 grains per U.S. gallon).

Tests were also made on the waters manufactured and sold by Carl H. Schultz as containing lithia. They were found to contain a little more lithia than claimed. *E.g.*, the formula on his "Vichy with Lithia," calls for an amount corresponding to about 57 parts LiHCO_3 per 100,000. The analyses showed 60 to 62 parts.

The results enumerated may be tabulated as above.

NOTES ON HIGH VACUA.*

By J. SWINBURNE.

I.

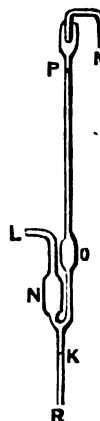
In a series of Papers on "Incandescent Lamp Manufacture," contributed to *The Electrician* in 1887, I called attention to the great superiority of the Geisler to the Sprengel form of mercury pump. Several kinds of Sprengel

pump were successively connected to a Geissler, and both were worked at the same time. The Sprengel invariably stopped taking air down before the Geissler, in fact the Geissler never stops. It acts as its own McLeod gauge, and never indicates a perfect vacuum. The probable reason why the merits of the Geissler have been so underrated is that it needs the greatest care in securing perfect dryness of the bulb and valve. Not only will traces of water-vapour condense under the floating valve instead of lifting it and going through, but it is probable air does so too. About a century ago Davy showed that if the mercury were allowed to run up gently in an imperfect Torricellian vacuum, a bubble was left; but if allowed to rise suddenly, it indicated a perfect vacuum, the air being condensed against the glass. In the lamp Papers I described a form of pump which avoids the difficulties due

FIG. 1.



FIG. 2.



to small condensations. The main bulb discharges into a small chamber sealed by a little V tube, so that a pressure of $1/100$ A would move the mercury. This chamber exhausts into a larger globe, exhausted mechanically and sealed by a floating valve. The small chamber is thus as thoroughly exhausted as an ordinary pump can pump it; but the pump proper, exhausting into high vacuum, can thus work better. The condensed air and water cannot expand back into it. It is thus really a double pump, or two mercury pumps in series. The only drawback is that it needs some pressure to open the first valve or sealing, so that there might, after all, be some condensation under it. I have lately devised and used a pump made as follows :—A (see Fig. 1) is the body or chamber of the pump proper. This exhausts into the small chamber B, sealed by the valve C, and this exhausts into the chamber G, sealed by the floating valve, H. G is connected to a reservoir and mechanical air-pump. The valve C has a long thin glass rod passing down through

* Read before the British Association for the Advancement of Science, Leeds Meeting, 1860, Section A.

A into the lower tube, which acts as a guide. A loose sleeve, F, is strung on this rod. There is a swelling at E which fits the lower end of the sleeve, and is small enough to pass through the neck in putting the pump together. When the mercury rises in the globe A it lifts the sleeve till the lower end catches on E, which closes it. The mercury rises and floats the sleeve, thus lifting the valve C. The mercury that sealed C then runs out, and there is a clear passage through into B; so no condensation takes place in A. The mercury rises till it floats H. When it falls, the valve C acts again, for the mercury has filled the sleeve F over the top, and C is heavy enough to sink the sleeve and rod when the sleeve is full of mercury. I have tried electro-magnetic and other arrangements, but this is the best as far as I have gone.

When using a pump it is best not to let air, and perhaps moisture, run through it more than can be helped. By the use of a sort of syphon it is possible to seal on new work to be exhausted without letting the air-pressure into the pump.

The point K (see Fig. 2.) is the barometric height at which the mercury normally stands in the tube R. There is then a clear passage between L, which is connected to the tubes to be exhausted, and M, which goes to the drying tubes and pump. When a tube has been sealed off and a new one is to be put on, the mercury reservoir at the foot of the arrangement is raised so that the bulb N is filled. A tap at the foot of the tube R is closed and the vacuum in L is broken. The mercury then runs up to the new barometric height P. The new tube is then sealed on and exhausted by a mechanical pump, the connection being then sealed off. The mercury in the long tube then stands only half an inch or so above that in N, and on opening the tap at the foot of R, the communication is made again to the pump. The small bulb O, and the trap at the top are to prevent a plug of mercury from going round into the phosphoric tubes.

The pump is driven by water so as to be self-acting, and can be left running for any length of time. Those who have worked much with mercury pumps will realise the value of this. Nothing makes one feel the futility of life more than to exhaust something by hand which cracks at the last stage, when five hours of life have been ticked off.

II.

In the same Papers on lamp-making I urged that the methods of measuring high vacua were inaccurate and completely misleading. The McLeod gauge and the induction coil are usually relied on for testing vacua. In incandescent lamp work the induction coil is almost exclusively used. With the test by induction sparks, I have at present nothing new to add, and will confine myself to the McLeod gauge. In measuring vacua with this gauge it is assumed that the mercury itself has no vapour tension. The vapour tension of mercury has been given by Regnault as about 50 millionths of an atmosphere. If it is anything like this, of course a vacuum of one millionth, or of 0.005 millionth, as some experimenters profess to have reached, is absurd. When discussing this subject, at the Society of Arts after Dr. S. P. Thompson's well-known Paper on "Mercury Pumps," Prof. Ramsay gave 0.25 millionth of an atmosphere, or, as I shall write it shortly, 0.25M, as the vapour tension of mercury at ordinary temperatures.

The whole action of a pump is consistent with a vapour tension of from 25 to 50M. A Geissler does not reduce the pressure in geometrical progression; but when it gets a good vacuum it takes out very little air each stroke, worked fast, and much more if worked slowly. This looks as if when the tension of mercury vapour was nearly reached, the air taken out at each stroke was what diffused into the mercury vapour. This would also explain why a Geissler, which goes on long after a Sprengel stops, does not so readily make a sparkless tube. A Sprengel stirs up the mercury, and gives the tube, being exhausted,

more chances of getting filled with mercury vapour, which is a non-conductor. This also explains why so many experimenters get better vacua with hot mercury. Of course a new pump should be heated to get the moisture off the glass, but not when it is in ordinary use.

To test this more directly I attached two McLeod gauges to the same pump. They communicated till a fair vacuum was reached. One was then sealed by raising the mercury past the elbow tube. The gauges were allowed to communicate by lowering the mercury every now and then, and it was always lowered before taking a reading. By this arrangement, when the pressure was reduced nearly to the vapour pressure of mercury, one gauge might have little but mercury vapour, and show a good vacuum; while the other had air at the same pressure, and showed a pressure equal to the vapour tension of mercury, or nearly so. The gauges are graduated by finding p corresponding to one-millionth of an atmosphere, and graduating accordingly. The pressure in millionths is then the product of the reading on the closed tube and the difference in the column. Each reading is thus readily taken at several pressures to make sure there is no condensation of any vapours or gases. The readings obtained varied in an extraordinary way. When the exhaustion was carried so far that the open gauge registered 2M or 3M, the closed registered from 20M to 60M. The least difference in temperature seems to make a large difference in the readings. In some cases, when the vacuum was still low, the open gauge was heated till the mercury sputtered, and condensed about the bulb. The bulb was then warmed to evaporate the mercury and drive all the air out, and the elbow tube sealed by raising the mercury. When the gauge was cool both were unsealed and readings taken. The gauge that had been warmed sometimes gave 1M against no less than 230M in the other. Ten minutes' connection generally brought the readings equal. Obviously the movement of the air need not depend on diffusion only; for a very small difference of temperature would cause mercury to evaporate in one gauge and condense in the other, driving the air with it.

I made a gauge with an alloy of about equal parts of potassium and sodium, which is liquid at ordinary temperatures. It would, of course, absorb any mercury vapour, and has probably a low-vapour tension. It was very troublesome, for it could not be exposed to the air for a moment, and heavy hydrocarbons would prevent the pump's working. The alloy always gets some moisture, and gets coated with a thin film of oxide which prevents drops from uniting, and they can only be run together by heating under a hydrocarbon of low boiling-point. I eventually got the gauge fitted up, but the alloy acted on the film of moisture on the glass, and the bubbles formed seemed to drive plugs of it about. It has a very low specific gravity, and pistons of it began to stray about inside the pump, and I was afraid they might get to the mercury, and by combining explosively, smash the pump, so the experiment was abandoned. In one experiment a plug of the alloy wandered into the mercury in R and cracked the tube.

Fusible alloy was next tried. It worked better, but the vapours of some sulphur that was used to trap any mercury vapour blackened the surface, and only two readings were obtained. These gave a pressure of only 13.5M as the vapour tension of mercury.

Whether it is really 13M or 50M is of comparatively little importance; but there seems to be quite enough evidence that the readings of 0.001M and higher vacua that have been given are inaccurate to the extent of some hundreds of thousands per cent. This is important in many investigations pursued by means of mercury pumps; for instance, experiments on the "Fourth State of Matter." The question is also important in lamp making, as it shows that better vacua are possible, and they may be an advantage. I do not know whether pumps worked with alloy of sodium and potassium will come into commercial use.

THE PRESENT POSITION OF THE HYDRATE THEORY OF SOLUTION.*

By SPENCER UMPREVILLE PICKERING, M.A., F.R.S.

It is but four years since this Section devoted a day to the discussion of the Nature of Solution;† since then, however, the general aspect of the question and the position of the advocates of the two rival theories have undergone such a complete change, that in renewing the discussion we shall run but little risk of going over the same ground which we then trod. At Birmingham, Dr. Tilden opened the discussion by passing in review all the well-known and long-known facts which might by any possibility throw some light on the nature of solution, and those who followed him in the discussion each gave the interpretation of these facts which harmonised best with his own views, and, as the facts themselves were susceptible of several different interpretations, the not surprising result followed that each disputant departed holding precisely the same opinions which he had brought with him. Since then, however, each party has obtained, or thinks that he has obtained, positive evidence in favour of his own views; evidence which, if upheld, must be accepted as conclusive, or which must be overthrown before his opponents can claim the victory. The supporters of the hydrate theory claim that the curved figures representing the properties of solutions of various strengths show sudden changes of curvature at certain points, which are the same whatever be the property examined, which correspond to the composition of definite hydrates, and which, therefore, can only be explained by the presence of these hydrates in these solutions; while the supporters of the physical theory, now identified with the supporters of the osmotic pressure theory, claim to have shown that, with weak solutions at any rate, the dissolved substance obeys all the laws which are applicable to gases, and that, therefore, its molecules must be uninfluenced by, and uncombined with, those of the solvent.

In another respect also I may notice that our position to-day differs considerably from what it was four years ago; for instead of having to argue the matter out amongst ourselves, as we did then, we are now favoured with the presence of some of those whose work in this very subject has made their names familiar household words with every physicist and chemist throughout the scientific world.

I propose in the first place to give a brief summary of the evidence which has lately been adduced in favour of the hydrate theory, and in the second place to inquire whether the conclusions drawn from this evidence are invalidated by the important facts elucidated by Raoult, van't Hoff, Arrhenius, and Ostwald.

In one respect the supporters of the hydrate theory start now under a distinct advantage, namely, that their most active opponents do not altogether deny the existence of hydrates in solution, although it is only in the case of strong solutions that they will admit their presence; in such solutions, indeed, it is difficult to see how their presence could possibly be denied. The only means which we have of proving that a liquid is a definite compound is by ascertaining whether its composition remains unaltered by its passage through the gaseous or solid condition—by fractionating it by means of distillation or crystallisation. With liquids of comparatively small stability, such as hydrates, crystallisation is the only method available; the results of crystallisation have led us to conclude that the liquid represented by H_2SO_4 is a definite compound, and precisely similar results must force us to accept the definiteness of the liquids $\text{H}_2\text{SO}_4\text{SO}_3$, $\text{H}_2\text{SO}_4\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4\text{H}_2\text{O}$; in the case of each of them the liquid freezes as a whole, and without change of composition; the temperature remains constant through-

out the solidification, and any excess of either water or sulphuric anhydride which may have been added may be separated from the pure compound, which alone crystallises from the mixture. Thus, in the instance taken, between the anhydride on the one hand and water on the other, we have four definite compounds, all existing in the liquid condition.

It does not follow, however, that every hydrate which exists in solution can necessarily be obtained in the solid condition; probably no solution, even when it possesses the exact composition of some existing hydrate, consists of that hydrate only, but of a mixture of it with the products of its dissociation (though the amount of these may be very small), and whether the hydrate or one of these dissociation products crystallises out on cooling must depend on the relative ease with which the bodies in question assume the solid condition; when the hydrate does not crystallise easily we can hope to obtain evidence of its presence by indirect means only.

Mendeléeff's conclusions respecting the densities of solutions of sulphuric acid and alcohol,* mistaken though I believe they were, led to the discovery of the means whereby such evidence might be obtained.

He stated that on plotting out the rate of change of the densities with the percentage composition of the solution (the first differential coefficient) he got a series of straight lines, forming figures with well-marked breaks, at points corresponding to definite molecular proportions; but on plotting out the experimental points which he said formed these figures, it is impossible to see any justification for this statement; in the case of sulphuric acid the points and Mendeléeff's drawing of them have been given side by side in the *Trans. Chem. Soc.*, 1890, p. 81, and in the case of alcohol they will be found in the *Zeit. f. Phys. Chem.*, vi., i., 10. Crompton then showed,† from an examination of Kohlrausch's values for the electric conductivity of sulphuric acid solutions, that a second differentiation might in some cases be necessary before rectilinear figures with breaks in them were obtained. In my own work on various properties of solutions of the acid I have made free use of this process of differentiation, but I have combined it with, and now nearly entirely rely on, an examination of the original curves with the help of a bent ruler.

In the *Phil. Mag.*, 1890, vol. i., p. 430, will be found rough sketches of the figures representing the densities, contraction on formation, electric conductivity, expansion by heat, heat of dissolution, and heat capacity of the solutions, and in the *Trans. Chem. Soc.*, 1890, p. 338, that representing the freezing-points. In some cases, such as the freezing-points of solutions of near 58 and 100 per cent. strength, a mere inspection of the figure enables us to locate the position of abrupt changes of curvature; in general, however, the recognition of such changes is more difficult. On attempting to draw any of these figures with the help of a bent ruler it was found that the whole figure could only be drawn in several sections, and it was also found that each section thus drawn consisted of a single curve of a parabolic nature, although a ruler, when bent by the pressure exerted by the two hands, by no means necessarily forms a parabola; and, moreover—and this is the most important part of the evidence—it was found that these figures, though differing so greatly in their general appearance, all split up into the same number of sections, indicating the existence of changes of curvature at the same points; and, further still, these points corresponded to solutions of definite molecular composition in all cases where the ratio of the acid to the water was sufficiently large to render any such comparison possible; the average difference between the composition indicated by the changes of curvature and that of definite hydrates was only 0.057 H_2O . With weak solutions it is, of course, impossible to assert that the changes occur at definite molecular proportions owing to the smallness of the change

* Read before the British Association for the Advancement of Science, Leeds Meeting, 1890, Section B.
† *Report*, 1886, p. 444.

* *Zeit. f. Phys. Chem.*, i., p. 275; *Chem. Soc. Trans.*, 1887, p. 77.
† *Chem. Soc. Trans.*, 1888, p. 116.

in percentage composition which would be caused by an additional molecule of water to each H_2SO_4 , but the changes with these weak solutions are of precisely the same character as those with strong solutions, and, unless some strong evidence to the contrary be forthcoming, we must attribute them to the same cause.

To discuss fully the value of the evidence thus obtained would take me more hours than I can now afford minutes; but I think that I may say that these results stand at present unquestioned and uncontroverted, and that unless they can be controverted we must accept the presence of hydrates in solution as having been proved. I may also add that my results with sulphuric acid solutions have been strengthened by obtaining analogous results with solutions of several other substances: that one of the hydrates indicated by them has been proved to exist by isolating it in the crystalline condition: and lastly, that a law governing the freezing-points of solutions has been formulated, according to which we can calculate within experimental error the freezing-point of any solution, whatever its strength may be, provided we acknowledge the existence of every hydrate which my work has indicated; whereas, if we deny the existence of these, the freezing-points calculated according to this or any other law show such divergences from the found values that all semblance of agreement disappears. I am indeed labouring under no small disadvantage in attempting to support the hydrate theory when the greater part of the evidence existing in favour of it is as yet unpublished.

Before proceeding to the second part of my subject I wish to draw attention to the great complexity of some of the hydrates which my work has indicated, as well as to the fact that the indications of sudden changes are nowhere more marked than they are with these very weak solutions. The changes, which are observed in the heat of dissolution curve from 5 per cent downwards,* afford a good illustration of this latter fact; or, again, the freezing-points of weak solutions may be instanced† where the rate of fall from 0 to 0.7 per cent is a quarter as great again as it is from 0.07 to 1.0 per cent. The complexity of the hydrates indicated is so great that in the extreme cases they must be represented as containing several thousand H_2O molecules, and the suggestion of such complexity will no doubt prejudice many against my conclusions in general—though on what grounds I know not, for we are entirely in ignorance at present as to the possible complexity of liquid molecules. It is interesting to note that a similar complexity of molecular grouping must be admitted if we accept Raoult's original statement that one molecule of any substance dissolved in 100 molecules of a solvent lowers the freezing-point of this latter by about 0.63° : for, if this be so, we must assign to the molecules of the various substances entered in the second column of Table I. the magnitude there indicated when they are dissolved in the solvent named in the first column, for it requires that proportion of these bodies to lower the freezing-point of 100 molecules of the solvent by 0.63° ; and, amongst these few instances which I have collected from my own determinations, we find molecular aggregates containing as many as 200 of the fundamental molecules, and even this number, I may mention, probably understates the complexity to a very considerable extent; for the depression in this and some of the other cases had to be estimated from that observed with solutions containing as much as 10 grms. molecular proportions to 100 of the solvent, and the molecular depression increased rapidly with the strength of the solution: 1000 H_2O would probably be a low estimate of the complexity of the molecules of water when dissolved in a large excess of the hexhydrate of calcium chloride, a complexity comparable with that of the hydrates, which my other work has indicated, and that too in the case of that very substance which these hydrates contain—water.

* Chem. Soc. Trans., 1890, p. 137
† Ibid., p. 343.

TABLE I.

Molecular Weights of Substances in various Solvents.*

Solvent	Dissolved substance producing 0.63° depression.†
100 $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	32 H_2O 63 H_2SO_4
100 $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$	8 H_2O 15 H_2SO_4
100 $(\text{CaNO}_3)_{24} \cdot \text{H}_2\text{O}$	90 H_2O 42 $\text{Ca}(\text{NO}_3)_2$
100 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	210 H_2O 63 CaCl_2

Now as to the question of how far the theory of osmotic pressure, and the results on which it is based, are antagonistic to the hydrate theory: and let me first define clearly the position which I take in this matter. I do not for one moment call in question any of Raoult's classical work, which is now so familiar to us, nor do I question that these results reveal the existence of a depression of the freezing-point which is approximately and generally constant; and I consequently admit that we can generally obtain an approximately correct value for the molecular weight of the substance by observing the depression which it causes; nor, again, do I wish to question the correctness of the mathematical relationship which van't Hoff and Arrhenius have shown to exist between osmotic pressure, the lowering of the freezing-point, and other properties, provided we accept the fundamental assumptions on which their calculations are based—the truly gaseous nature of dissolved matter, and the dissociation of salts into their ions. But what I do question is that the facts of the case warrant such assumptions, and that the constancy and regularity of the results are so rigorous as to justify the conclusion that the solvent has no action on the dissolved substance, and that there are no irregularities such as would be caused by the presence of hydrates.

According to the osmotic pressure theory, the dissolved matter, so long, at any rate, as it is not present in greater quantity than it would be in the same volume of its gas, if it were gasified under normal conditions, is really in the gaseous condition, and obeys all those laws which apply to gases. According to the hydrate theory this will be but partially true. That the dissolved substance is in a condition comparable with that of a gas in so far as the separation of its own particles from each other is concerned, must be admitted—indeed, I arrived independently at this same conclusion from a study of thermo-chemical data—but inasmuch as there is present the solvent, which we believe is *not* an inactive medium, its molecules cannot have the same freedom as if they were truly gaseous, and will, therefore, obey the laws of gases imperfectly only.

It will be well to confine our attention to but one of those properties connected with osmotic pressure, and to select for that purpose the one which has been most fully investigated—the lowering of the freezing-point of a solvent: and the tests which may be applied to ascertain whether in producing this lowering the dissolved substance behaves as a perfect gas or not, may be grouped under three principal headings:—

1. Is the molecular depression (i.e. that produced as calculated for one molecule dissolved in 100 molecules) constant independent of the nature of the solvent?
2. Is it independent of the strength of the solution, so long as this strength does not exceed the limits ("gas" strength) above mentioned? (Boyle's law.)
3. Is it independent of the nature of the dissolved substance? (Avogadro's law.)

In the *Phil. Mag.*, 1890, vol. i. p. 495, will be found instances of the variation in the molecular depression which may be noticed by altering the solvent (see also Table I. above). With water in six different solvents it varied

* Other instances of high molecular weights are mentioned by Brown and Morris (*Chem. Soc. Trans.*, 1888), and Gladstone and Hibbert (*Phil. Mag.*, 1889, vol. ii., p. 38).

† Determined from the freezing-points of very weak solutions.

FIG. 1.—DEVIATION FROM REGULARITY OF THE FREEZING-POINTS OF VERY WEAK SOLUTIONS.

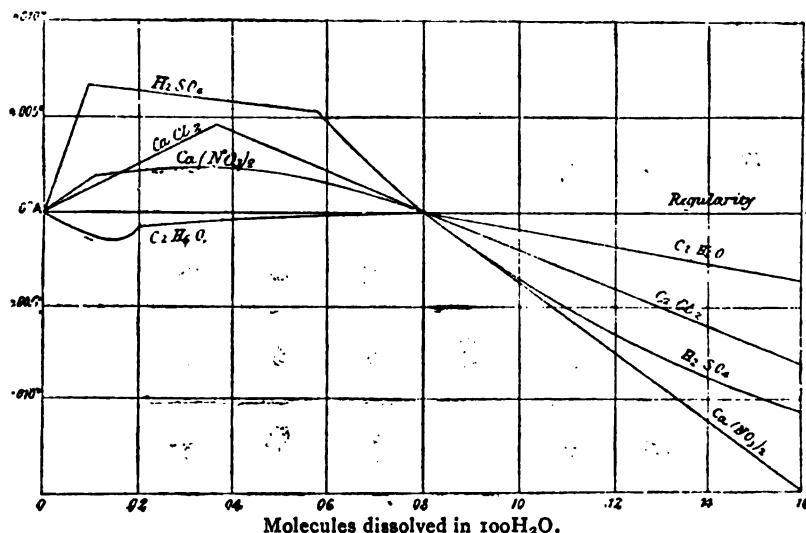
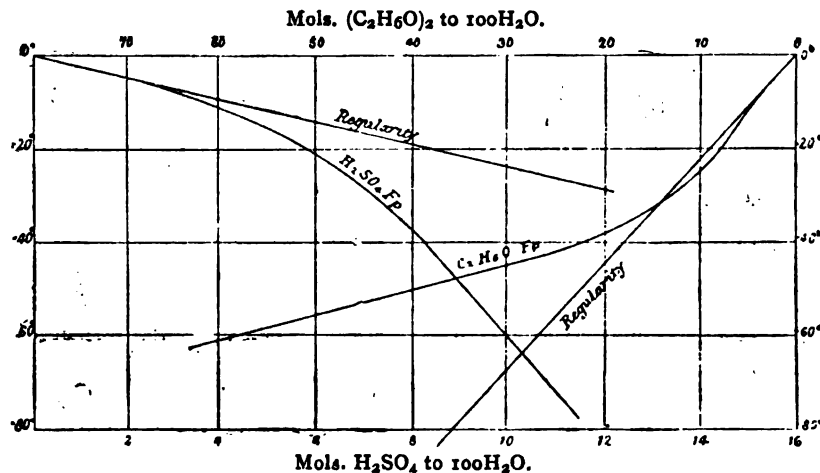


FIG. 2.—FREEZING-POINTS OF SULPHURIC ACID AND ALCOHOL SOLUTIONS.



between 1.072° and 0.003° ; with sulphuric acid in four different solvents between 2.15° and 0.01° ; with calcium chloride in two different solvents, from 2.773° to 0.01° ; and with calcium nitrate in two solvents, from 2.5° to 0.015° ; while many instances may be collected from Raoult's data showing that the same substance which acts normally in one solvent may act abnormally (give only half the usual depression) in another. Such variations are so great—from 100 to 35,600 per cent.—that there can be no doubt but that the solvent is *not* that inert medium which the supporters of the physical theory would have it to be, but that it has a very great influence on the results obtained. It must be noted, however, that this objection, though applying to Raoult's original views, does not, or, at any rate, may not, apply to van't Hoff's theory, for, according to this theory the nature of the solvent has an influence in determining the lowering of the freezing-point, W in van't Hoff's equation,—

$$\Delta T = \frac{0.02 T^2}{W},$$

representing the heat capacity of the solvent. But the lowering is according to this equation independent of the nature or the amount of the dissolved substance, so that the two following objections will apply to van't Hoff's theory as well as to Raoult's statement.

Secondly, as to the influence of the strength of the solution. It is remarkable that although the osmotic pressure theory depends on the behaviour of solutions below a certain strength, no attempt whatever has been made by its supporters to obtain any data respecting such solutions. The data on which their views were founded referred to solutions considerably stronger than the requisite "gas strength," and though, no doubt, it was convenient to work with data which afforded a ready excuse for any awkward irregularities which might be met with, such data must lack the conclusiveness which is so eminently desirable. The few data which I have accumulated as to solutions of an "ideal" strength can leave no doubt that, even in their case, the depression is not a constant independent of the strength.

A solution of sulphuric acid containing $0.08\text{H}_2\text{SO}_4$,

100H₂O would be of a strength comparable with the gas from the acid if it could be gasified at normal pressure and temperature, and the molecular depression should be constant for all solutions below this strength: it should be represented by a horizontal line such as AB in Fig. 1, whereas the observed deviations from constancy are very great, being represented by the lines marked H₂SO₄; and, moreover, these deviations are by no means regular, and cannot therefore be attributed to imperfect gasification; they possess none of the characteristics of the deviations of gases from Boyle's law. The determinations on which these results are based are very numerous; there are about sixty experimental points on the portion here shown, and the mean error of each point as determined in two different ways was only 0.0005°, a quantity represented by one-tenth of one of the divisions of the paper; and the deviations from the regularity amount to thirteen times this quantity, and to as much as 16 per cent of the total depression measured.

The other lines in Fig. 1 represent the deviations from regularity in the case of calcium chloride, calcium nitrate, and alcohol respectively, and these, though they are smaller than in the case of sulphuric acid, are far too great to be attributed to experimental error; and the fact that they occur sometimes in one direction, sometimes in the other, precludes the possibility of attributing them to any constant source of error in the instruments used or in the method adopted.

Remembering that these are the only data which we have at present respecting very weak solutions, we must conclude that the hypothesis that such solutions exhibit perfect regularity is wholly untenable.

It is important to observe that when we pass on to stronger solutions, where the actual magnitude of the deviations becomes so great that they would be revealed by the roughest experiments—deviations of even 70°—and where, I believe, even the supporters of the osmotic pressure theory would not hesitate to attribute them to the disturbing influence of hydrates; these deviations occur in precisely the same irregular manner as they do in the case of weak solutions, and must evidently be attributed to the same cause. The results with alcohol given in Fig. 2 illustrate these irregularities in a very striking manner. It must also be pointed out that, apart from the irregularity of these deviations, their very direction shows that they cannot be attributed to the dissolved particles being brought within the sphere of each other's attraction, as in the case of the deviation of gases from Boyle's law, for the result of this would be that their attraction on the particles of the solvent would be diminished and the freezing-point of this latter would consequently be lowered to an abnormally small extent, whereas precisely the reverse is the case in nearly every instance at present investigated: the freezing-points of strong solutions are abnormally low. Various instances of this will be found in the *Phil. Mag.*, 1890, vol. i., p. 500, that of sulphuric acid, which is illustrated here in Fig. 2, being by no means the most prominent; while the case of alcohol, now for the first time displayed (Fig. 2), is the only exception which has, so far, been met with, and that is an exception only in the case of excessively strong solutions.

From the instances above mentioned, some answer may be obtained to the third question, whether the molecular depression is independent of the nature of the dissolved substance. The values obtained with these four substances, taking solutions of a strength corresponding to that of their gases, are:—

Calcium chloride		2.850°
Calcium nitrate		2.744°
Sulphuric acid		2.313°
Alcohol		2.180°

a variation of 30 per cent, which must give an emphatic denial to the idea of absolute constancy; and if we take instances from other substances, where the data available

refer to solutions of somewhat greater strength, we find that the very substances on which the idea of constancy was originally founded show variations reaching 60 per cent (*Phil. Mag.*, 1890, vol. i., p. 492), while in other cases, which I have quoted elsewhere (*loc. cit.*, p. 493),* the variation attains the still larger dimensions of 260 per cent.

To every one, therefore, of the three test questions as to constancy and regularity, the experimental results give an unhesitating negative.

In the instances quoted above the depression actually found for alcohol has been doubled in order to simplify the comparison of it with the other substances. Alcohol belongs to that class of bodies which give just half the value in water that the majority do, and of which there are some instances in the case of every solvent yet examined. The explanations which the supporters of the chemical and physical theories give of these half values differ so radically from each other that it is hopeless to attempt to arrive at any agreement as to the nature of solution till this difference is settled. The chemists say that these half values are in all cases the abnormal ones, just as Raoult did originally, and explain them by representing the molecules of the dissolved substances which give them to consist of two fundamental molecules. The physicists give exactly the same explanation in the case of every solvent except water, but in this case they say that the smaller values are the normal ones, and the larger the abnormal, the double magnitude of these being caused by the dissociation of the dissolved molecule into its two ions, whereby two molecules or acting units are formed from every one originally added.

(To be continued).

NOTICES OF BOOKS.

Book D; or, Arithmetical Physics. Part I. B. Acoustics, Light, and Heat (Degree and Honours Stages). By C. J. WOODWARD, B.Sc. London: Simpkin and Marshall. Birmingham: Cornish Brothers.

THIS work is most distinctly examinational, and as such it must excite in the mind of the critic, not "alarm," but regret and disappointment. We feel anxious to know the real value of the method of teaching chemistry and physics which the author is carrying out in his series of "Educational Works." We feel very dubious in how far it can train the student in the art of observing rightly and of drawing correct inferences from the phenomena thus observed. We fear that this system of teaching science is one of the many results of examinationism. We cannot by any examination questions hitherto devised test the power of the student in detecting phenomena, observing them correctly, and tracing them to their causes. Hence examinationists, if they must teach the physical sciences, enter upon a bye-path better suited to their entire system. We fear that this is a mere trifling with the demand for scientific education. The first point surely should be to perfect the student as an observer; the second, to train him up in the art of tracing effects to their causes, or rather, perhaps, of harmonising the phenomena observed. But this does not lend itself to the examinational system. Hence the demand of the age is evaded. We entertain grave doubts whether works of the type in question are calculated to train students either in the acute observation or in the accurate interpretation of phenomena. But if the examinational system is to be retained at all hazards, they will, of course, have their value.

* The depression produced by H₂O in 100H₂SO₄ is 1.07° instead of 0.07° as there given.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—A circular, signed by Messrs. F. J. Lloyd and F. L. Teed, has been sent round to the members of the Chemical Society. It calls attention to the fact that the Fellowship of the Society has in the past been given to persons who have very small title to be considered chemists. The circular goes on to state that in consequence of this action on the part of the Electors of the Chemical Society, the Fellowship, regarded as a professional qualification, has fallen into disrepute, and is likely in the future to become less and less considered as an evidence of its holder's scientific training and ability.

To remedy this state of affairs, it is proposed that in future more stringent regulations shall be enforced by the present members, which shall exclude the election of any candidates for the Fellowship unless they can show what may be considered, on broad grounds, suitable qualifications; and by the general tone of the circular, it is evident that these suitable qualifications are intended to be of a scientific nature, and not the more ordinary qualifications as to character and ability to pay the Society's subscription.

I hope that you will afford me room to express some objections which I hold to the position Messrs. Lloyd and Teed have taken on this question.

The chief advantages which the Chemical Society offers to its Fellows may, I think, be found in the admirable Journal, the library, and the opportunity afforded for the reading and discussion of papers, and for intercourse between men interested in the science of chemistry; it was for these or similar purposes that the Society was formed, and I believe it was never intended that its Fellowship should be in any way regarded as a scientific qualification. The chief object was the advancement of the science. Now, the library and, above all, the Journal, which improves, one might almost say, from month to month, cannot be conducted without money, and as this money is obtained from the subscription of the Fellows, any limitation of their numbers on any other ground than that of character and financial ability to pay the subscriptions is, from this point of view, most unwise. If people having small, or even absolutely no, scientific qualifications, but who are able to pay their subscriptions, and do not fall short of the ordinary requirements as to character, wish to become members of the Chemical Society, it is certainly an advantage rather than otherwise to the scientific member who appreciates his Journal and the library.

It is no doubt quite true that persons having practically no knowledge of chemistry have joined the Society merely with the intention of using the mystic letters F.C.S. as an advertisement. This is an abuse, and several courses of action which might be taken to nullify the evil readily suggest themselves. The method proposed in the circular will certainly not succeed. Action of this kind will confirm the position of any unqualified persons who may already be Fellows. The Chemical Society having committed itself to the policy of considering the conferment of its Fellowship as a recognition of scientific training (for this is what the proposed action must do), individuals of this class already holding it will benefit immensely: unless, indeed, it is proposed to proceed to the drastic measure of turning out present members, a course which I presume is hardly contemplated. It is, perhaps, not generally known that there is at present no legal means by which any person can be prevented from placing the letters F.C.S. after his name, and, moreover, as any one can become a Fellow of the Berlin Chemical Society by merely paying his subscription, he is then able to place

F.C.S. Berlin, after his name, which probably will have quite as much, or perhaps even greater, weight with the outside public than the more sober F.C.S. It is particularly for the protection of the outside public that these new regulations are proposed. The scientific man knows very well how to take care of himself.

If means are taken to make it as widely known as possible that the Fellowship of the Chemical Society is no guarantee whatever of the attainments of the holder, the resignation of some few who look upon its possession as having a merely commercial value in return for their £2 per annum, may follow; but the many who, as students or amateurs, would be excluded by the more rigorous tests proposed will remain members, and it is sincerely to be hoped that in the future they will, as they have done in the past, continue to join the Society. Surely persons sufficiently interested in chemistry to value the Chemical Society's Library and Journal possess all the qualifications which should be required for the spread and advancement of the science.

If there were any danger that the class of persons to whom the circular refers could at any time obtain a management of the affairs of the Society it certainly would be a matter of the greatest importance: but surely a danger of this kind cannot be seriously considered as ever likely to occur.

Lastly, what class of persons can consider themselves aggrieved if the Fellowship of the Chemical Society comes to be no longer considered as a qualification? The pure scientist or professional man of any status depends to a certain extent perhaps upon his college degrees, but chiefly upon his actual position, the practical or theoretical work he has undertaken, and upon his past record generally. The practical analyst or technologist has the Institute of Chemistry, which gives a qualification that cannot be assumed by outsiders without they lay themselves open to legal action, which the officers of the Institute would be prompt to initiate. The Institute has been formed to discharge the very functions with which now it is sought to burden the Chemical Society (which has very different aims and duties). The qualifications demanded by the Institute from applicants for the Associateship or Fellowship are not unduly stiff, certainly not more so than those required from the medical student before he is permitted to practise. In short, chemists who are interested in this matter will do well to exert themselves to uphold the Fellowship of the Institute of Chemistry as being a guarantee of scientific training; whilst every means must be taken to spread among the public the knowledge that the Fellowship of the Chemical Society is no evidence whatever (nor was ever intended as such) of an individual's training or capacity.—I am, &c.,

ARNOLD PHILIP.

Royal Indian Engineering College,
Cooper's Hill, Oct. 4, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 11, September 15, 1890.

On the Equivalent of Gadolinia.—Lecoq de Boissaudran.—The equivalent of gadolinia has been determined by M. de Marignac as about 120.5 ($\text{SO}_3 = 80$); that is, 156.75 for the atomic weight of Gd, and 361.5 for the molecular weight of Gd_2O_3 . The result of the author's approximate analysis of the gadolinia of M. de Marignac does not greatly modify these values, as the two chief impurities (Sm_2O_3 and Zr_2O_3) of the gadolinia in question exist

in it in almost equal proportions (about $\text{Sm}_2\text{O}_3 \frac{4.4}{100}$ and $\text{Zr}_2\text{O}_3 \frac{4.7}{100}$), and have molecular weights situate the one above and the other below the molecular weight of the total mass ($\text{Sm}_2\text{O}_3 = 348.0$; Gd_2O_3 (of Marignac) = 361.5 , $\text{Zr}_2\text{O}_3 = 367.0$ approximately), yielding a partial compensation of the effects of these impurities. On applying the result of the author's analysis, and setting out with the mean equivalent 120.5 , we obtain for the true gadolinia contained in the earth of M. de Marignac, equiv. = 120.79 , and $\text{Gd} = 157.19$, but these values seem a little too high. In spite of the small quantity of material available, the author attempted to take the equivalent of the gadolinias of his fractionations Nos. 6 and 9. A known weight of the earth was converted into sulphate and weighed, after exposing the salt to a dull red heat. On operating upon small masses (0.2 grm.) such as the author was obliged to use, the errors in weight, due to the absorption of air and moisture by the crucibles and their contents, are sometimes very important, unless special precautions are taken. It is useful to study the progress of the weights of the crucible, first empty and then full, and to deduce from the curve of these observations the value of the absorption exerted by the material from the extinction of the fire until the weighing. He thus obtains:—

No. 6. First Experiment.

	Equiv.	At. weight.
1. By weighing Gd sulphate	119.69	155.53
2. By BaOSO_3 obtained from such sulphate	120.04	156.06
Mean of first experiment ..	119.86	155.80

No. 6. Second Experiment (better than first experiment).

By weighing Gd sulphate	119.84	155.76
Meant for earth No 6	119.85	155.78

No. 9. (Good Experiment).

By weighing sulphate	120.08	156.12
Mean for Nos. 6 and 9	119.96	155.95

The slight impurities still contained in Nos. 6 and 9 should slightly reduce the equivalent, and, consequently, the mean experimental atomic weight, = 155.95 , would be a little increased if the earth were absolutely purified. According to estimations which are probably exaggerated, this additional value would scarcely raise the atomic weight of true Gd by 0.39 . The author thinks that the atomic weight of gadolinium will differ little from 156.15 , unless the experimental value of 155.95 involves some notable error. Prof. Clève has determined the equivalents of several successive portions obtained by fractionation with ammonia, but as his object was to know if gadolinia could or could not be split up into various earths having decidedly different equivalents, he had no inducement to take exceptional precautions to obtain a degree of accuracy higher than that which sufficed for his purpose. The following are the numbers found by Prof. Clève for some of his fractions:—

	Atomic weight.
First fraction, deeply coloured	154.15
Fourth „ pale yellow	155.28
Fifth „ nearly white	155.1
Sixth „ white	154.77

The observations of Prof. Clève thus agree fairly with those of M. de Marignac.

The Acetic Ether of Diacetyl-carbinol.—A. Combes.—The author has obtained a compound, $\text{C}_5\text{H}_8\text{O}_3$, of an acid odour, of powerfully reducing properties. It reduces Fehling's liquid and ammoniacal silver nitrate in the cold, and does not furnish metallic derivatives.

Revue Générale des Sciences Pures et Appliquées.
Vol. i., No. 13, August 15, 1890.

Gay-Lussac.—A biography of this illustrious chemist which appears in connection with the inauguration of a statue to his memory, at Limoges, on August 11th.

MISCELLANEOUS.

Appointments.—Sir Charles Cameron, Professor of Chemistry and Hygiene, Royal College of Surgeons, Ireland, has been appointed a member of the Army Sanitary Committee by the Secretary of War. The members of the Committee now number seven. They have to consider the sites, &c., of barracks, upon which £4,000,000 are to be expended.—Mr. J. Morrow Campbell, B.Sc., F.C.S., Assistant to Professor Sexton at the Glasgow and West of Scotland Technical College, has been appointed Assistant Engineer and Analyst to an expedition proceeding immediately to Persia, under the Persian Bank Mining Rights Corporation, Limited. Mr. Campbell is succeeded at the College by Mr. T. S. Goodwin, formerly Chief Assistant to Prof. Watson at the Anderson's College Medical School.

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DAVID LEWIS, Treasurer.

Treasurer's Chambers, 20, York Place,
Edinburgh, October 8, 1890.

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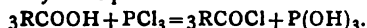
THE CHEMICAL NEWS.

VOL. LXII. No. 1612.

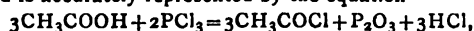
THE ACTION OF PHOSPHORUS TRICHLORIDE ON ORGANIC ACIDS AND ON WATER.*

By C. H. BOTHAMLEY and G. R. THOMPSON.

THE interaction of phosphorus trichloride is given in almost all the text-books on organic chemistry as a general method for the preparation of the acid chlorides, and is represented by the equation—



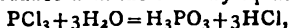
Some years ago Thorpe showed (*J. Chem. Soc.*, 1880, p. 186) that the action of phosphorus trichloride on acetic acid is accurately represented by the equation—



but this work, being contained in his memoir on specific volumes, and not separately indexed, seems to have escaped attention, and the old erroneous equation is given in the most recent books. The authors confirm Thorpe's result, but find that the equation only holds good within certain narrow limits. In presence of excess of acid or of phosphorus trichloride secondary reactions take place, and in almost all cases a small quantity of Leverrier's yellow oxide, P_4O_6 , is obtained. Propionic acid and butyric acid gave a precisely similar result, but the quantity of P_4O_6 formed and the general tendency of the reaction to be complicated by secondary changes increases with the molecular weight of the acid.

Benzoic acid and phosphorus trichloride yield hydrochloric acid and benzoyl chloride, but the quantities are lower than those calculated from the equation, and the character of the residue shows that secondary reactions have taken place to a considerable extent. It is not improbable that in this case some phosphorous acid is formed. Direct experiment showed that phosphorous acid and benzoyl chloride interact, with formation of benzoic acid and hydrochloric acid, and there can be little doubt that several reactions take place simultaneously.

The action of phosphorus trichloride on water takes place in accordance with the ordinary equation—



so long as the water is in considerable excess; but if the chloride is in excess it reacts with the phosphorous acid with formation of hydrochloric acid and yellow phosphorus oxide mixed with other oxides, and in some cases with free phosphorus. It is probable that phosphorous oxide, P_4O_6 , is first formed, but afterwards decomposes. In the interaction of water and excess of phosphorus trichloride the authors obtained the soluble form of P_4O_6 or P_4OH in the cooler parts of the vessel, but if exposed to a temperature above 70° it became insoluble, a result which agrees with an early statement of Gautier.

The authors consider that their results prove that in the interaction of phosphorus trichloride and monobasic organic acids the fundamental change is represented by the equation—



As soon, however, as any acid chloride and phosphorous oxide are formed they may interact with the still unchanged acid and phosphorus trichloride, especially if one of the latter is in excess. They may also interact with one another. In the acetic series the tendency to produce secondary changes increases with the molecular

weight of the acid, probably because of the more ready interaction of the acid and the phosphorous oxide. In the case of benzoic acid the secondary changes take place to a very considerable extent. Where, as in the action of phosphorus trichloride on acetic acid, the products are very volatile, and are rapidly removed from the sphere of action, there is very little opportunity for secondary changes to occur, but in other cases equilibrium is established between the many possible reactions, and the extent to which any given change takes place is determined by the conditions, and especially by the temperature.

The action of phosphorus trichloride on organic acids cannot be regarded as a good general method for the preparation of acid chlorides. It gives satisfactory results only in the case of the lowest members of the acetic series.

This investigation is being continued.

The Yorkshire College, Leeds.

THE SULPHUR WATERS OF YORKSHIRE.*

By C. H. BOTHAMLEY.

THE sulphur waters of Yorkshire divide themselves geologically and chemically into two groups. The springs of one group come to the surface at intervals along a great anticlinal in the Yoredale beds, which stretches from near Clitheroe in Lancashire to beyond Harrogate; but they occur in greatest number and volume at Harrogate, which is built on the summit of the anticlinal. The springs of the other group are found at different points in an alluvial formation, which lies at the foot of magnesian limestone between the river Don and its tributary the Went, and which is in many places covered with a thick layer of peat. They occur in greatest number and volume at Askern.

The Harrogate waters rise from a considerable depth and are free from organic matter. In some cases they contain more than 14 parts of dissolved saline matter per 1000, about 12 parts being sodium chloride. The remainder of the solid matter is chiefly calcium carbonate and calcium and magnesium chlorides. It follows, therefore, that the Harrogate sulphur waters are of a highly chlorinated character. Sulphates are absent; bromides, iodides, and lithium are present in minute quantities. One of the most remarkable constituents is barium, the quantity of barium chloride in some cases being twice as great as the total quantity of solid matter in the best potable waters supplied to our largest towns. The volume of dissolved hydrogen sulphide amounts in the Montpellier Strong Sulphur Well to nearly 80 c.c. per litre.

The Askern waters rise from no great depth, and may almost be regarded as surface waters. They contain only about 2 parts of dissolved solid matter per 1000, the greater part being calcium carbonate and calcium and magnesium sulphates. Chlorides are present in very small quantities. Traces of iodides are present, but potassium, lithium, barium, and bromine could not be detected in 5 litres of the water. The whole of the hydrogen sulphide present is in the free state, and amounts in the strongest waters to about 50 c.c. per litre. There can be little doubt that the hydrogen sulphide results from the reduction of the sulphates; but exactly how this reduction is brought about has not yet been determined.

The latest complete analyses of the Old Sulphur Well and the strong Montpellier Sulphur Well at Harrogate will be found in *J. Chem. Soc.*, 1881. The Askern waters have not been examined for nearly fifty years. The investigation of these waters is still in progress, and

* Abstract of a Paper read before the British Association, Leeds Meeting, 1890, Section B.

* Abstract of a Paper read before the British Association, Leeds Meeting, 1890, Section B.

it is hoped that the results will be published in detail before the end of the year.

The Yorkshire College, Leeds.

NOTES ON THE VULCANISATION AND DECAY OF INDIA-RUBBER.*

By WILLIAM THOMSON, F.R.S.Ed., F.C.S.

UNDER ordinary conditions india-rubber for vulcanising is usually mixed with sulphur and heated to a high temperature, when chemical combination takes place between the sulphur and the rubber, producing a much more valuable compound for ordinary purposes than unvulcanised rubber; the former remaining soft at very low temperature and firm at high temperatures, whilst the latter becomes hard and quite plastic respectively at those temperatures.

In making cloth for waterproof garments another method is employed for vulcanising the rubber—viz., by wetting its surface with a mixture of somewhere about 5 to 10 parts of chloride of sulphur dissolved in 100 parts of bisulphide of carbon, and then heating the fabric gently to evaporate away the excess of these substances. The rubber-covered cloth cannot be heated to a high temperature like the rubber alone, because the heat would be liable to injure the cotton, silk, or wool of the fabric, or destroy or injure the colours.

The bisulphide of carbon softens and penetrates the fine layer of rubber, carrying with it the chloride of sulphur dissolved in it, and it is generally supposed that the chloride of sulphur breaks up the sulphur combining with the rubber, producing vulcanisation, and the chlorine combining with the hydrogen producing hydrochloric acid, which is liberated. This reaction is clearly not the correct one, and it is probable that the reverse is more in accordance with the facts—viz., that the chlorine of the sulphur chloride combines with the rubber, producing vulcanisation, leaving the sulphur in the free state or only partially in combination with the rubber, because in rubber vulcanised by the cold process I have found free sulphur to be present.

From a piece of rubber-covered cloth I separated the rubber and submitted it to analysis by mixing it thoroughly in small pieces with pure sodium carbonate and igniting, then dissolving the whole in water, and adding to it peroxide of hydrogen previously treated with excess of barium chloride (to separate sulphuric acid or sulphates.) The peroxide ensures the conversion of the lower oxides of sulphur into sulphuric acid, whilst the excess of barium chlorides precipitates the sulphuric acid in the solution, which is then weighed as barium sulphate.

Another portion of the made-up solution was neutralised and the chlorine present titrated. The rubber previous to ignition, as above described, had been well boiled in water and dried to separate any hydrochloric acid which might be present, but only a faint trace of chlorine compound could be thus separated from the rubber.

The total sulphur present in the rubber amounted to 2.60, and the total chlorine to 6.31 per cent.

The yellow-coloured sulphur protochloride is best adapted for vulcanising because it does not act too strongly upon the rubber, whilst the dark coloured chloride of sulphur, containing as it does a large quantity of the higher chlorides of sulphur, is liable to render the rubber quite hard by vulcanising it too much. The theory generally adopted to explain this is, that these higher chlorides break up easily, liberating their sulphur, which thus combines in greater quantity with the rubber; but my experiments and analyses prove that it is chiefly the

chlorine and not the sulphur of the chloride of sulphur which produces the vulcanisation.

A rubber substitute much used at present is produced by acting on vegetable oils, such as rape, linseed, &c., with a mixture of chloride of sulphur and bisulphide of carbon. The oil becomes converted into a solid substance resembling india-rubber to some extent, but being much more brittle. This body is now used in large quantity for mixing with india-rubber for the purpose of cheapening its production. On analysis of some samples of this material I have invariably found that it contained a much greater proportion of chlorine than of sulphur, and this process, therefore, is a vulcanisation by chlorine rather than by sulphur.

Recently I analysed three samples of rubber substitute, the one termed "special," another "spongy" india-rubber substitute, the third being similar to the first in appearance. The first contained of sulphur 3.4 and of chlorine 7.6 per cent; the second contained of sulphur 4.56 and of chlorine 8.22, and the third 2.67 of sulphur and 7.90 of chlorine per cent.

These rubber substitutes contain considerable quantities of oily matters soluble in ether, which I have also found to be chlorine and sulphur compounds of the oils. The first yielded 20.0 per cent, the second 14.3, and the third 11.5 per cent of these thick oily matters soluble in ether. This oily substance from the first sample contained 2.6 per cent of sulphur and 6.1 per cent of chlorine, whilst that from the second contained 2.97 and 6.87 per cent of sulphur and chlorine respectively.

Some rubber manufacturers regard this oily matter as injurious to the rubber and reject any substitute which contains any considerable proportion of it. I have found, however, by experiment that this oily compound instead of acting injuriously on india-rubber, actually acts as a preservative of it; some rubber threads were smeared with this oily extract, some with ordinary (unvulcanised) rape oil, and some left untreated: these were put into an incubator at 150° Fahrenheit for a few days, when it was found that the oil-treated rubber was quite soft and rotten, whilst the other two had remained sound; after a few days more, the original rubber threads had become quite rotten, whilst the threads smeared with the oily part of the vulcanised oil remained quite sound.

The first and second samples of rubber substitute were examined for soluble chlorides or hydrochloric acid, by boiling in water; the first gave 0.18 per cent of chlorine soluble in water and the second 0.05 per cent.

It has been known for some time that copper salts exert a most injurious influence on india-rubber; copper salts are sometimes used in dyeing cloths which are afterwards employed for water-proofing with india-rubber, and it seems quite astonishing what a small amount of copper is required to harden and destroy the rubber, and the destructive effect of copper is further enhanced if the cloth contains oily matters in which the copper has dissolved.

As an example, here is a piece of cloth alleged to have damaged the thin coating of india-rubber on it: I found it to contain copper, and with a view of demonstrating this point, I took one piece in its original condition; to the end of this I pasted a similar piece of the cloth from which the oily and greasy matters had been removed by ether, and to the end of this again I pasted another piece of the same cloth from which I had removed both oily and greasy matters and copper; these three pieces joined end to end into one were then coated in the usual way with india-rubber, and then hung in an incubator at 150° F.; in the course of a few days the rubber on the original cloth had become soft, and it then hardened and became rotten and useless; the second piece from which the greasy matters had been removed then became quite hard and rotten, whilst the part from which both greasy matters and copper had been removed has remained in a perfectly elastic and good condition.

Professor Dewar observed accidentally that metallic

* Read before the British Association, Leeds Meeting, 1889, Section B.

copper when heated to the temperature of boiling water in contact with the rubber exerted a destructive effect upon it. With a view of finding whether this was due to the copper *per se* or to its power of conducting heat more rapidly to the rubber, I laid a sheet of rubber on a plate of glass and on it placed four clean discs, one of copper, one of platinum, one of zinc, and one of silver; after a few days in an incubator at 150° F., the rubber under the copper had become quite hard, that under the platinum had become slightly affected and hardened at different parts, whilst the rubber under the silver and under the zinc remained quite sound and elastic. This would infer that the pure metallic copper had exerted a great oxidising effect on the rubber, the platinum had exerted a slight effect, whilst the zinc and silver respectively had had no injurious influence on it. A still more curious result was this, that the rubber thus hardened by the copper contained no appreciable trace of copper; the copper, therefore, presumably sets up the oxidising action in the rubber without itself permeating it.

I have pleasure in acknowledging the assistance rendered to me in this investigation by my assistant, Mr Frederick Lewis.

ON THE UNBURNED GASES CONTAINED IN THE FLUE GASES FROM GAS STOVES AND DIFFERENT BURNERS.*

By WILLIAM THOMSON, F.R.S.Ed., F.C.S.

I HAVE been working for some time with a view of determining whether the gases escaping as flue gases from gas stoves and different burners were really free from gas capable of combustion, such as carbon monoxide, or unburned hydrocarbons or hydrogen. I spent some time in trying to separate and determine the quantity of carbon monoxide present, if any; but this problem was beset with so many difficulties that for the moment I abandoned it, and contented myself for the present with determining the quantity of unburned carbon and hydrogen in whatever forms these might exist.

For this purpose I arranged an apparatus consisting of two carefully weighed U-tubes filled with strong sulphuric acid and two weighed U-tubes filled with soda-lime, through which the flue gases were first passed; these absorbed the water and carbon dioxide contained in the flue gases, leaving the hydrocarbons (not absorbed by vitriol), hydrogen, and carbon monoxide to pass through a red-hot glass tube filled closely to the extent of 15 inches with oxide of copper prepared *in situ* from copper wire gauze. The gases were then passed through strong sulphuric acid and soda-lime contained in previously weighed U-tubes, and the results were calculated on the gas, measured at 60° F. and 30 inches barometric pressure, from the measure of gas drawn into the aspirator (treated as water-saturated gas); the carbon dioxide and water vapour absorbed in the tubes being then added on, making up the measure of flue gas originally employed, and which was taken for the determination.

The coal-gas employed was previously passed through large cylinders filled with calcium chloride to dry it before combustion, and at the same time as the experiment was going on, and side by side with it, was estimated the carbon dioxide and water vapour present in the air itself by passing it by means of another aspirator through strong sulphuric acid and soda-lime in U-tubes previously weighed.

The carbon dioxide in the air itself ranged from 0.41 to 0.66 grain per cubic foot of air, and the water from 3.51 to 7.23 grains in the same volume.

The amounts of carbon dioxide and water collected from the flue gases, after deducting the quantities actually present in the air, were taken as those due to the combustion of the coal-gas.

The standard I employed was the one used by Professor Roberts-Austen in his analysis of the flue gases from the burning of coal, and the apparatus employed was generally similar to that also employed by him.

The carbon and hydrogen left unburned were measured in terms of 1000 parts of carbon actually derived from the combustion of the gas in the stove or burner.

The total quantities of carbon dioxide and of water in the flue gases amounted to from 6.6 to 10.8 grains per cubic foot for the former and from 5.6 to 10.5 grains of the latter in the same volume.

The amount of flue gas passed in each experiment was about one cubic foot, and although the variations were considerable, the general results were conclusive in showing that the combustion of gas when burned in gas stoves for heating purposes is much more incomplete than one might be led to suppose.

The only burner in which the weight of the tubes remained constant after passing the burned gas, and in which the combustion was presumably complete, was in a paraffin-oil lamp in which the flame was not turned to its highest point. In another experiment with the flame turned full on, 12.04 and 3.09 respectively of carbon and hydrogen escaped combustion per 1000 of carbon completely burned.

The next nearest approach to complete combustion was in an Argand burner, in which all the carbon was completely burned; but an amount representing 0.2575 part of hydrogen escaped combustion per 1000 parts of carbon completely burned, whilst in a second experiment 0.113 of carbon and 2.5414 of hydrogen escaping combustion were registered per 1000 parts of carbon completely burned.

Then came one of Bray's ordinary flat flame burners, burning 4 cubic feet per hour, which gave 11.12 of carbon and 0.95 hydrogen unburned per 1000 of carbon completely burned.

Following in order these results, came the Welsbach light, in which the gas heats to whiteness a tube or mantle composed of a filmy thickness of the oxides of zirconium and titanium, the mantle being surrounded by a glass tube similar to that used in some paraffin-oil lamps. In this case the unburned carbon exceeded in amount the unburned hydrogen, there being 15.486 of the former and 3.794 of the latter per 1000 of completely burned carbon.

Three experiments were made with a Marsh-Greenall's heating stove, in which three Bray's luminous burners were employed. The first was made with a consumption of 5.62 cubic feet of gas per hour, when 12.6 and 3.0 parts of carbon and hydrogen respectively were registered per 1000 parts of carbon completely burned. The second experiment, with a consumption of 5.74 cubic feet per hour, gave 37.6 and 11.8 respectively of carbon and hydrogen unburned. The third experiment, with an increased consumption of gas (7.1 cubic feet per hour), gave 97.4 and 12.1 of carbon and hydrogen respectively unburned.

Two experiments were made with one of T. Fletcher's heating stoves, in which eight Bunsen burners play upon some fancy metal work (iron coated with magnetic oxide). The one experiment, in which the amount of gas passing was not measured, gave 43.3 of carbon and 24.6 of hydrogen unburned per 1000 of carbon completely burned. In the second experiment, where 6.81 cubic feet of gas were burned per hour, 66.3 and 20.0 respectively of carbon and hydrogen unburned were registered.

One experiment was made with one of T. Fletcher's stoves, in which twenty Bunsen burners play on asbestos projecting from a fireclay back, with a consumption of 8.14 cubic feet of gas, 138.9 and 11.7 parts respectively of carbon and hydrogen per 1000 parts of completely burned carbon were found.

In a stove in which the hot gases rise to the top of a cylinder filled with pipes (through which cold air passes

* Read before the British Association Leeds Meeting, 1890, Section B.

to be heated), and from the bottom of which the burned gases escape, after having cooled to a considerable extent, upwards of 200 parts of carbon escaped combustion per 1000 parts of carbon completely burned.

I have to thank my assistant, Mr. Harry Bowes, for the careful manner in which he performed the delicate and difficult experiments from which the above results were obtained.

THE PRESENT POSITION OF THE HYDRATE THEORY OF SOLUTION.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

(Concluded from p. 188).

If Raoult's views as to the constancy of the molecular depression can be maintained, the data themselves are conclusive against making this exception in the case of water; for, since the substances which give the lower values are supposed to act normally, it is evident that, if the values given are in any way abnormal, this abnormality must be due to the solvent. Now the values certainly are abnormal; they are about 1.03° , whereas the normal value for one molecule dissolved in 100 molecules of other solvents is 0.63° , and the excess can, therefore, only be explained by assuming that the molecules of water are more complex than those of other solvents in the proportion of 1.03 to 0.63 , or $1\frac{1}{4}$ to 1 ; in other words, the water molecules must be $1\frac{1}{4}\text{H}_2\text{O}$. This view cannot be reconciled with the atomic theory.

Indeed the theory of dissociation into ions is altogether unintelligible to the majority of chemists. It seems to be quite irreconcilable with our ideas of the relative stability of various bodies, and with the principle of the conservation of energy. Of course we know that each ion when dissociated is not supposed to be permanently dissociated, but to be continually combining with its neighbours and separating again from them as in every other case of dissociation; but at any particular moment a very large proportion of them is supposed to be free; a proportion which, according to the very results under discussion, must be very nearly, if not quite, 100 per cent of the whole; and we have to settle whether it is probable or possible that a decomposition such as this could have been effected by introducing the compound into water. And how can we regard it probable that compounds of such stability and compounds formed with such a development of heat as sulphuric or hydrochloric acid should be thus entirely dissociated by water; still less that these, and all the most stable compounds which we know, should be thus demolished, while all the less stable ones—such as hydrocyanic, sulphurous, boric acids, &c.,—remain intact? How can we admit that the more stable a body is, the more prone it is to be dissociated?

And if such a dissociation has occurred it must have been without any absorption of heat, and, consequently, energy must actually have been created. Take one of the simplest instances, that of hydrochloric acid. If anything at all is certain about atoms, it is that the atoms in an elementary molecule are united very firmly together, and that therefore in separating them a very large absorption of heat would occur. To separate 2HCl into 2H and 2Cl would absorb far more than the 44,000 cal. which we know are absorbed in separating 2HCl into H_2 and Cl_2 . Yet the supporters of the dissociation theory would have us believe that this separation has actually taken place, not only without any absorption of heat, but actually with a development of 34,630 cal.; that is, that—

$$44000 + 34630 + x \text{ cal.}$$

have been created, and that, too, through the intervention of the water, which has *ex hypothesi* no action whatever.

* Read before the British Association for the Advancement of Science, Leeds Meeting, 1890, Section B.

This difficulty is realised by the supporters of the physical theory, but the way in which they meet it does not appear to me in any way to overcome it. To explain the non-absorption of heat in the dissociation of the salt, they suppose that a charge of electricity combines with the liberated atoms, and, in doing so, evolves an amount of heat exactly equivalent to that absorbed in the separation of the atoms from each other. And a later development of the theory is, I believe, that the atoms, though separated, are still held together by means of these charges, so that the net result is the supplanting of the chemical bond by an electrical bond of a precisely similar value. It appears to me that nothing substantial is gained by such a substitution, and that its occurrence is not merely hypothetical, but impossible. Whence come these electric charges, and by what agency are they brought into play? On what grounds can it be maintained that a charge can combine with matter so as to evolve heat, and that the heat so liberated is always exactly equal to that absorbed in the decomposition of the compound? If this quality exists, how can we account for the force which develops one overcoming the equal force which develops the other? And how, again, can we account for the heat developed in the act of dissolving? If, on the other hand, the heat of the combination of these charges is supposed to be equivalent to the heat of combination of the atoms, plus that of the heat of dissolution, we are met by the objection that the latter is often negative, and that, therefore, the heat of the combination of the charges must often be less than that of the combination of the atoms, so that the lesser force must be regarded as overcoming the greater.*

That free ions exist in solution is supposed to have been proved by a recent observation of Ostwald's to the effect that these ions may be separated and brought into different parts of the liquid by the proximity of a charged body. The separation of the ions is, of course, recognised by the subsequent liberation of hydrogen, oxygen, acid, alkali, &c., and it is certain that on allowing these to mix and combine heat will be developed and the salt solution re-formed; and thus, by replacing and removing the charged body, it would evidently be possible to produce an unlimited amount of heat. Now, if the charged body has lost none of its charge, and if mechanical energy has not been expended, this heat must have been created, and the whole groundwork of physical science must be false; whereas, if energy in any form has been expended on the solution, the experiment proves nothing, for there is nothing to show that this energy has not been utilised in bringing about the very dissociation the previous existence of which was in question.

I have already shown that the experimental data prove the absence of that constancy and regularity which ought to exist according to the physical theory, and to place the hydrate theory on unassailable grounds it is only necessary to show that the deviations from constancy and regularity are of a magnitude such as might reasonably be assigned to deviations due to the presence of hydrates. That variations of 260 and 36,000 per cent in the value of the depression—such as are observed by altering the dissolved substance or the solvent respectively—are amply sufficient to satisfy the most exalted views of the influence of chemical attraction, requires, I think, no demonstration, and we may therefore content ourselves with examining the deviations observed when the proportions of the solvent are altered—such deviations as are illustrated in Fig. 1.

It cannot be maintained that the energy of the chemical combination of, say, water with sulphuric acid, is the only reason why the temperature of the mixture of these two must be cooled below 0° before any of the latter will crystallise out; some lowering of the freezing-point will be

* On the view that hydrates exist in solution, there is no difficulty, as I have shown elsewhere, in explaining the absorption of heat during dissolution without violating the principle of the conservation of energy.

TABLE II.—Freezing-points of Solutions of Sulphuric Acid.

I. Per cent H_2SO_4 .	II. Mech.	III. Phys.	IV. Chem.	V. Total.	VI. Found F.-p.	Next hydrate.	
						VII. Calc. Per cent.	VIII. Found. Per cent.
0.068	0.0209	0	0.0110	0.0347*	0.0354	0.37	0.36
0.362	0.1114	0.0004	0.0248	0.1508*	0.1582	1.43	1.06
1.06	0.3275	0.0014	0.0589	0.4314*	0.4272	3.54	4.02
4.02	1.285	0.071	0.077	1.582*	1.59	8.40	8.59
8.59	2.879	0.388	0.189	3.815*	3.80	18.17	18.49
18.49	6.96	3.23	1.59	11.78	11.83	29.7	29.5
29.53	12.85	18.82	3.50	34.17	34.00	37.5	37.7

* The actual total has been increased by 10.4 per cent of its value to give the figures quoted in these five cases, for reasons which will be given elsewhere. Some of the numbers in this table may be subject to slight corrections, as they have been quoted in the absence of the original calculations.

caused by the mere interposition of the foreign molecules of sulphuric acid between those of the water, and on certain grounds, which I have explained elsewhere,* I estimate the mechanical lowering, as I term it, at 0.56° for each dissolved molecule to 100 of the solvent (a molecule of solvent water being $3H_2O$), a value which, it may be noted, is not far removed from Raoult's experimental value of 0.63°. There is also another source of lowering depending mainly on the heat capacities of the substances concerned, which I term, for convenience, the physical lowering; but its value, in the case of weak solutions, is very small, and I need, therefore, say no more about it here. Both these lowering causes would exist whether there were hydrates present or not; but if these were present we should get a further depression due to their existence. Any given hydrate would have to be decomposed into the next lower one before it could give up any water for crystallisation, and a certain amount of resistance would thus be offered to this crystallisation, to overcome which the solution would have to be further cooled. The necessary cooling may be estimated in the following way:—Supposing the solution to be a mixture and to be cooled below its normal freezing-point; then, on solidification, the temperature would rise to this point; but if this solidification involved a chemical decomposition which absorbed x cal. the rise of temperature would be thereby reduced, the reduction thus caused amounting to $x \div$ the heat capacity of the solution. As the heat absorbed in the decomposition of the various hydrates of sulphuric acid is known, we can calculate the lowering produced by their presence.

In Cols. II., III., and IV., Table II., I have given the depression due to the three above-mentioned causes in the case of certain solutions, Col. V. containing their sum; and it will be seen what a small proportion of this total lowering can be attributed to purely chemical causes. With most solutions it does not exceed 10 per cent of the total, and with weak solutions, such as are generally used in freezing-point determinations—say 5 per cent—it amounts to considerably less than 0.1°; this, too, in the case of sulphuric acid, where the heat of formation of the higher hydrates is greater than with any other known substance.

The reason, therefore, why the deviations from constancy are so small as to have escaped detection hitherto, and the reason why solutions behave almost as if their chemical nature was non-existent, becomes apparent; but this near approach to constancy and regularity, instead of proving the correctness of the physical theory, and giving a death-blow to the chemical theory, is really one of the strongest arguments which can be adduced in favour of the latter. If the hydrate theory is right, the influence of hydrates must often be nearly inappreciable.

But it is not only a general concordance between the found and calculated magnitude of their regularities which the hydrate theory is capable of affording, but a concordance so exact that the precise value of the deviation at

any point may be calculated. In Col. VI. of Table II. are given the observed freezing-points of the solutions, and these show an average difference of but 0.004° for the three weaker solutions, and 0.06° for the four stronger solutions, from those calculated (Col. V.). The last two columns exhibit this concordance in a different manner; from the observed freezing-point we can calculate the composition of the hydrates which must exist in the solution (Col. VII.), and these are found to agree so fully with those indicated by the examination of the curved figures representing various properties of the solution (Col. VIII.) that the maximum difference between the two is only 0.48 in the percentage of acid present.

When we can by simple calculations, based on one series of determinations, prove that the hydrates in solution must be the same as those which totally independent experiments have led us to suppose, we have, I think, arrived at a proof as nearly absolute as it is possible to conceive; and, if I have succeeded in showing that this proof may be accepted without in any way rejecting the facts on which the advocates of the osmotic pressure theory rely—approximate constancy, approximate regularity, and approximate similarity between dissolved and gaseous matter—I shall feel that I have done far better work than the mere establishment of the hydrate theory, by pointing out a possible *modus vivendi* for both theories almost in their entirety, and by helping to break down that wall of separation between physicists and chemists which is fast crumbling into dust.

THE MANUFACTURE OF COLOURLESS TANNINS.

By A. VILLON.

THE author employs the following method for obtaining colourless tannins from tanning drugs, such as chestnut wood, quebracho, sumac, valonia, dividivi, oak-wood, &c.

It comprises three chief operations: lixiviation of the tanning matters, precipitation of the tannin in the state of an insoluble tannate, and the separation of the tannin.

The lixiviation of the tannin wares presents nothing particular; it is the methodic system with six becks acting in a current of carbonic acid at the temperature of 80°–90°. In this manner liquids are obtained at from 5½ to 11° Tw., according to the nature of the ware employed. The liquor is passed on into settling vats, where it is allowed to cool. When it has arrived at the temperature of the atmosphere it is allowed to flow into a refrigerating apparatus, similar to those employed in breweries, i.e., a vat fitted with a worm in which there circulates the uncongealable liquid of a freezing-machine.

The temperature is thus lowered to + 2°, at which point it is kept for half an hour. The extractive matter and the tannin which are insoluble in the cold are precipitated, and are separated by passing the liquors through a filter-press. To render this clarification more complete there

is added 0.5 per cent. zinc sulphate. The tannin contained in the liquid is then titrated and its weight in the mass submitted to one operation is calculated.

Per kilo. of tannin thus found the author adds to the liquid 2½ kilos. pure crystalline zinc sulphate previously dissolved in five times its weight of hot water. The liquid is transferred into a vat fitted with an agitator, into which is then passed a current of gaseous ammonia, derived from the decomposition of 2½ kilos. ammonium sulphate (by means of lime) to each kilo. of tannin existing in the liquid. The vat is entirely closed and the excess of ammoniacal gas passes into another vat.

The ammonia displaces the zinc oxide which combines with the tannin to form a zinc tannate insoluble in a neutral or an ammoniacal solution. During the passage of the ammoniacal gas the liquid is raised to ebullition by means of a steam worm. Hence, merely zinc tannate is precipitated. The liquid is passed into a filter-press and washed first with hot ammonia water, then with cold, and lastly with cold water. On leaving the filter-press the clear liquid is passed into cast-iron pans, where it is saturated with milk of lime so as to give off ammonia, which serves in a following operation.

The zinc tannate is stirred up in five times its volume of water and decomposed with dilute sulphuric acid, when zinc sulphate is formed and tannin is set free. Then separate the zinc sulphate from the liquid, a solution of barium sulphide is gradually added until no further precipitation takes place. A double decomposition takes place between the two salts, with the formation of insoluble zinc sulphide and barium sulphate. The precipitate is filtered off and the tanning liquid is ready for use.

The precipitate is treated with dilute sulphuric acid when the zinc sulphide is dissolved, yielding zinc sulphate which serves for succeeding operations, and sulphuretted hydrogen which is given off and which is utilised. There remains barium sulphate, which is separated from the zinc sulphate by filtration. The barium sulphate may be reconverted into barium sulphide by ignition with carbon. Calcium sulphide may be used in place of barium sulphide. Copper sulphate may be substituted for the zinc salt, but the process is more costly if any loss occurs in the treatment. In this manner we may obtain directly extracts of tannin at 14°–22° Tw., containing 20 to 30 per cent of tannin free from extractive matter and almost colourless. —*Bulletin de la Société Chimique de Paris.*

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, October 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined, the whole were found to be clear, bright, and well filtered.

The improvement manifest in London water supply on or about the middle of August, and to which we have already directed attention, has been more than fully maintained during September. The colour-tint of the Thames-derived water during the first half of August was as brown to blue 20:20; during the latter half of August as 14:1:20; whilst during September the average colour-tint was 11.5:20. The same fact is clearly indicated by a comparison of the results furnished by the oxygen test. Thus, whilst during the month of August an average of 0.065 grain of oxygen was required per gallon, during September only 0.044 grain of oxygen was needed. These results show an unbroken purity of supply, even under the severe conditions consequent on flood, and an almost unprecedented rainfall.

The marked uniformity in the composition of the various waters during the past month is specially noteworthy. Further, the complete freedom of the numerous samples examined from any trace of suspended matter is to be remarked.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

ON AN APPARATUS APPLICABLE FOR GAS ANALYSIS AND OTHER PURPOSES.*

By W. E. ADENEY, F.I.C., Assoc.R.C.Sc.I.,

Curator and Examiner in Chemistry in the Royal University, Dublin.

THE apparatus which forms the subject of this paper was originally designed to serve the double purpose of collecting and determining the gases incident to water analysis. In practice, however, it has been found applicable for a number of other purposes, including gas analysis by absorption and combustion, the analysis of carbonates, of nitrates, and of organic matter by the permanganate method; it may also be employed as an air-pump, and for distillation *in vacuo* or under reduced pressure.

The form of the apparatus is shown in the figure. It consists of a gas burette, A, enclosed in a glass cylinder, B, 75 m.m. in diameter, a barometer tube, C, which may also be employed as an open pressure tube, and a laboratory vessel, D. The whole apparatus is supported on a wooden stand.

The lower portion of the burette is contracted and passed through a hole cut in the centre of the india-rubber bung, E, which closes the lower end of the glass cylinder. It is then bent at right angles and joined to the pressure tube at A by a piece of india-rubber tubing, lined with canvas, and firmly wired to the tubes; and the joint is protected from the air in the ordinary way by fitting round it a piece of wide glass tubing, and filling the annular space formed with glycerin.

The way in which the glass cylinder, burette, and pressure tube are supported and held in upright positions will be understood from the drawing; it need only be mentioned that the wooden block which carries the cylinder, or rather on which the bung E rests, is cut away at the centre and side to allow the cylinder and burette to be placed in position, and that the upper portion of the

* Read before the Royal Dublin Society, June 18, 1890.

burette is held in its place by the brass plate *b*, one end of which is bent at right angles and screwed to the stand, and the other end is bent and cut to fit and clamp the upper part of the stop-cock as indicated in the drawing. By this means the burette is clamped firmly, but sufficient play is afforded for contraction or expansion of the glass by alteration of temperature.

The supply of mercury to the burette and pressure tube is regulated by means of a reservoir which can be raised or lowered by a pulley and small windlass, *c*, fixed to the back of the stand. The flexible tube from the reservoir passes through a hole in the back of the stand at *d*, and is attached to the pressure tube by means of the small side tube *e*. The necessity of attaching the connecting tube from the reservoir to the pressure tube, and not directly to the burette, will be explained later on.

The height of mercury in the pressure tube is read off by means of a millimetre scale etched on the unsilvered surface of the narrow slip of looking-glass, *f*, which is fixed close to the back of the pressure tube and inclined to the vertical plane, as shown in the drawing, so as to reflect the image of the tube from the portion of the glass bearing the scale. To read the height of the mercury in the tube the eye is held a little to the right of the scale, and moved about a little until the scale lines in the immediate vicinity of the reflected image of the mercury meniscus coincide with their images reflected from the silvered surface of the glass. When the eye is in this position the height of the mercury can be accurately read to 0.5 m.m., and with aid of a lens to about 0.25 m.m.

The burette and pressure tube are each provided with a Friedrich's patent glass stop-cock of the pattern shown in the drawing. Two branch tubes, *g*, *h*, spring from the stop-cock of the burette; the former is a capillary tube, and serves to connect the burette with the laboratory vessel and other purposes, while the latter is of wider bore (2 to 3 m.m.) and is intended to connect the vessel containing the substance to be examined with the burette. The two tubes are firmly held against the wooden block *k*, which is grooved to receive them, by a brass plate lined with cork and screwed to the said block. It is necessary to support the two tubes thus to obviate the danger of their being broken off from their junction with the stop-cock by a sudden blow or undue pressure. When firmly held in the manner described, the tubes will bear even considerable pressure without any danger of being broken, and, as will be explained afterwards, when the laboratory vessel is fixed in position for working, a decided pressure is exerted against the tube *g*.

The contracted portion of the burette immediately below the stop-cock is about 225 m.m. long, and has a capacity of 15 c.c.; the wider portion is about 410 m.m. long, with a capacity of about 250 c.c. Both portions are graduated, the former at intervals c.c., of 1 and the latter at intervals of 25 c.c.

The pressure tube is 1000 m.m. long; and since it can be employed both as an open and closed tube, a volume of a gas may be measured under a pressure equal to 1500 m.m. of mercury, or, on the other hand, under as low a pressure as 1 m.m. Thus the apparatus is more sensitive than Thomas's (*Chem. Soc. Journ.*, xxxv., 217).

The laboratory vessel differs in principle and shape from the one employed in Frankland's or Macleod's apparatus. The cylindrical portion, *n*, is 25 m.m. internal diameter and 55 m.m. long, and is furnished with the side tube, *o*, for connecting the vessel with an independent mercury reservoir; the portion *p* is 45 m.m. in diameter and 100 or 190 m.m. long, according to the character of the analysis to be made; this portion of the vessel, which is shown in the drawing, has a length of 100 m.m., the most useful size for water analysis. The upper part, *q*, which has an inverted conical shape, is 55 m.m. long, the diameter decreasing from 20 m.m. at the mouth to 4 m.m. at its narrowest part. Two platinum wires are sealed into the vessel in the positions shown in the drawing.

The particular shape given to the portion *q* allows the laboratory vessel to be easily connected or disconnected with the tube *g*. When the laboratory vessel is placed in position, as represented in the drawing, the tube *g*, the end of which is fitted in an india-rubber collar, tightly closes the narrow part of *q*, while the lower shoulder of the vessel rests upon the shelf *r*, which, in plan, has somewhat the shape of an inverted U. If the space above the collar be filled with water of mercury, a perfectly air-tight joint is obtained. The joint, in fact, may be made so staunch that, when the vessel is arranged in the manner described below, a torricellian vacuum may be maintained in it. When it is desired to disconnect the laboratory vessel, its lower portion is drawn forward sufficiently to clear the shelf, and is then lowered to detach it from the tube *g*. By reversing these movements the laboratory vessel may be again attached to the apparatus. The shape of the india-rubber collar is of importance; its lower end must be rounded off. It may be conveniently made in the laboratory from the core obtained by cutting a hole in an ordinary cork, by means of a cork-borer of suitable diameter; one end of the core will generally be found sufficiently rounded to suit the required purpose.

For some problems in gas analysis the laboratory vessel may be employed in the ordinary way. The lower and open end is immersed in a mercury trough, and may be filled from the trough in the following manner. The stop-cock is opened to the tube *h*, and the reservoir raised until the burette is full of mercury; the stop-cock is then turned to open to the tube *g*, and consequently to the laboratory vessel. The reservoir is now lowered slowly, and as the level of the mercury in the burette sinks, it rises in the laboratory vessel. The reservoir is lowered until the laboratory vessel is full. The air that is drawn into the burette during the operation is driven out into the atmosphere by opening the cock to the tube *h*, and again raising the reservoir. When the burette is full of mercury, the glass cylinder filled with water, and the pressure tube in proper order, the apparatus may be used in a similar manner to that of Frankland or Macleod.

Since the apparatus, however, can be employed as an air-pump similar in principle to Friedrich's new pump, as well as for measuring and analysing gases, its applicability to a great variety of purposes becomes possible, if the laboratory vessel be furnished with the means of filling it with mercury, as well as of adjusting the level of mercury in it, independently of the burette. This may easily be effected by closing the lower end of the vessel with an india-rubber cork, and connecting it by means of the side tube *o* to an independent adjustable reservoir which is raised and lowered by means of a pulley and windlass, *m*, fixed to the back of the stand, just as in the case of the reservoir furnished for the burette and pressure tube.

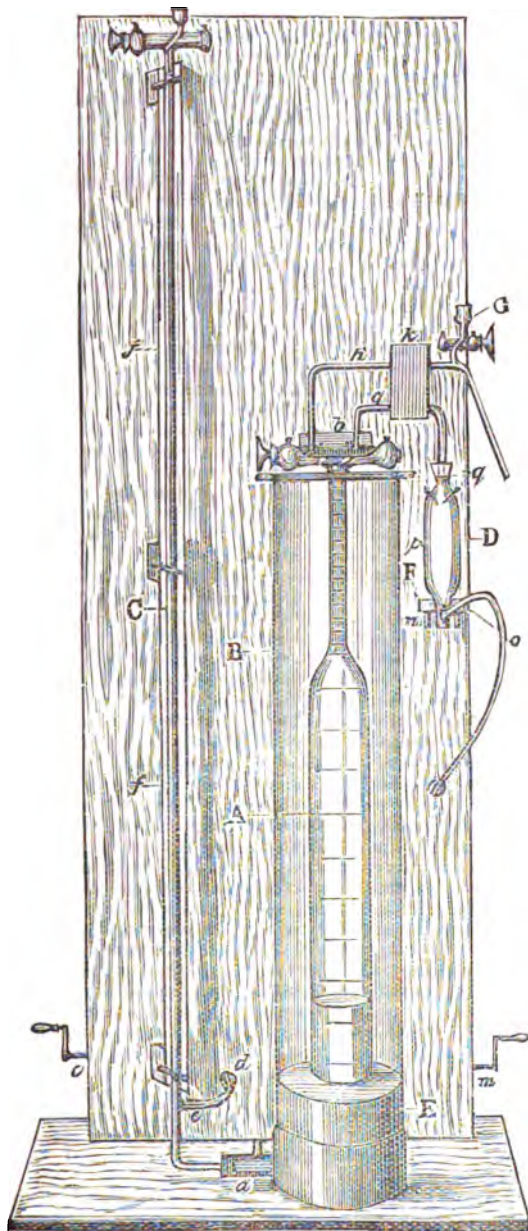
To provide the means for introducing reagents into the laboratory vessel, when it is modified as here described, the cork which closes the lower end of the vessel is fitted with a glass tube (which for the purpose of reference may be called the reagent) about 10 c.m. long, and 2 m.m. bore, one end of which is drawn out to a fine point, and the other end is bent at right angles, and has attached to it a piece of stout india-rubber tube about 15 c.m. long, and 1 m.m. bore. When the cork is fixed in its place, the fine point of the reagent tube projects into the interior of the vessel for about 2 c.m. A small Bunsen screw clamp is also provided with which to close the india-rubber tube when necessary.

The apparatus and stand should be permanently set on a small table of such a height that the mercury reservoirs may be lowered some 36 inches below the level of the lowest scale mark on the burette.

The heights of the mercurial columns corresponding to the different divisions of the burette are determined in the ordinary way with the aid of a kathetometer.

To calibrate the burette, it is filled with water in the following way:—The burette and glass tube *g* are first filled with mercury by raising the reservoir; a beaker con-

taining water is then held under the open end of *g*, and the reservoir lowered until the burette is filled with water down to the lowest division line. The beaker is now replaced by a small tared flask, and the reservoir slowly raised until the next division on the burette is reached by the mercury; the water displaced is received into the tared flask, and weighed; a similar operation is repeated for each division on the scale of the burette. Finally, the



capacity of the tube *g* is measured. During the process of calibration the wide glass cylinder which surrounds the burette is filled with water in order to maintain the water in the burette at a constant and known temperature.

During the analysis of a mixture of gases, all measurements are carried on with the level of the mercury in the burette adjusted to the same division line. The selection

of the division line must naturally depend on the volume of the gas to be analysed, and the object of the analysis.

An arrangement for accurately adjusting the level of the mercury in the burette at the division line selected for making measurements may be made thus:—A piece of white paper having a horizontal black line drawn upon it, is gummed to the stand behind the glass cylinder, and at the same level as the division line, an exact adjustment being made with the aid of a kathetometer. A similar arrangement may be made for each division line on the burette, but, generally speaking, it will only be found necessary for the 10, 15, 50, and 100 c.c. lines. With this arrangement the mercury may be adjusted to the level of a division line by the operator, with the naked eye, even more accurately than with the kathetometer, the operator being very much aided by the magnifying effect that the water in the cylinder has upon the burette, and upon the line gummed to the back of the stand.

The method of working the apparatus will be understood from the following description of the analysis of a water residue:—The residue is mixed with copper oxide, and packed in a combustion tube with oxide of copper and metallic copper; and the open end of the combustion tube is drawn out and shaped according to the directions given by Frankland and Armstrong in their method for the determination of the organic carbon and nitrogen in waters. The combustion tube may be directly attached to the tube *h* of the apparatus, but it is more convenient to interpose between them a U-shaped connecting tube, in the bend of which a bulb is blown for collecting the water formed during the combustion of a residue. The connections are made with pieces of india-rubber tubing protected with water jackets in the ordinary way, to prevent diffusion of air through them.

The burette and pressure tube, let it be supposed, are full of mercury, the stop-cock of the latter closed, and the laboratory vessel detached from the apparatus. If now the cock of the burette is opened to the combustion tube, and the reservoir lowered, air will pass from the combustion tube into the burette as the mercury flows out of the latter; when the mercury has reached the lowest level practicable in the burette, the stop-cock is turned to close connection with the combustion tube, and to open to the tube *g*, and the reservoir is raised to re-fill the burette with mercury and expel the air that has been drawn into it into the atmosphere. If, when the burette is again full of mercury, connection with the combustion tube be for a second time opened, and the cycle of operations described be repeated, a further quantity of air will be drawn from the combustion tube, and will be expelled from the apparatus. After several such repetitions the quantity of air remaining in the combustion tube will be inappreciable.

The degree to which the exhaustion has been pushed may be accurately determined by first filling the burette with mercury, and then, the stop-cock being closed, lowering the reservoir sufficiently to sink the mercury in the burette to the level of the 100 c.c. division line; a torricellian vacuum will consequently be obtained in the burette. Connection with the combustion tube is now opened, and the tube is gently warmed. After a few minutes the stop-cock is again closed, and the reservoir raised; if any air has been drawn from the combustion tube, its presence will be indicated as the mercury rises to fill the burette, and its volume may be accurately determined. With a little care it is quite possible to exhaust so completely the combustion tube, that no residuum of air can be detected in it by the method here described. The time required to exhaust a combustion tube, with the apparatus of the size described in this paper, is about ten minutes. The time, however, will vary somewhat with the dimensions of the combustion tube.

The combustion tube, after being exhausted, is heated to ignite the water residue, the stop-cock being closed during the process of heating.

During the combustion the laboratory vessel should be

carefully and completely filled with mercury, and attached to the apparatus in the following manner:—The laboratory vessel is held in a slanting position, with its lower shoulder just resting on the front edge of the shelf, *r*, and its upper part, *q*, loosely fitting round the collar at the end of the tube, *g*. The reservoir is then adjusted so that the mercury in it, when the laboratory vessel is full, shall be just above the level of the collar. The mercury slowly fills the laboratory vessel, and when it *has risen* a little above the collar, the lower shoulder of the vessel may be pushed into its place. After the laboratory vessel has been properly attached, the reagent tube must be freed from air. This may be done by unscrewing the Bunsen clamp, and allowing a little mercury to flow out of the tube. When the air has been completely driven out, the reagent tube is again closed by screwing up the clamp. If, after first attaching the laboratory vessel, any traces of air are detected in it (and small bubbles are especially liable to collect under the india-rubber collar attached to the tube *g*), the operator will be able to expel them by drawing the lower part of the vessel forward, and then lowering the vessel slightly to loosen its connection with the tube *g*. If the reservoir has been previously adjusted to the level of the end of the tube *g*, immediately on loosening its connection with the vessel in the manner described, the bubbles of air will escape into the atmosphere. After the laboratory vessel has been finally placed in position, a mercury trough filled with water, and supported on an ordinary table support, is placed under the vessel, and fixed at such a height that the lower end of the vessel is immersed in the water. This arrangement prevents leakage or diffusion of air through the india-rubber cork which closes the end of the vessel.

When the combustion of the water residue has been completed, the combustion tube is again exhausted, and gases resulting from the combustion are transferred to the laboratory vessel; this operation being completed, the gases are next passed into the burette to be measured.

The method of adjusting the level of the mercury in the burette, after the gases have been passed into it, will require some explanation. The simple plan of closing the stop-cock, and then raising and lowering the reservoir, in order to bring the mercury to the level of the division line selected for measurement, cannot be followed, since after transferring the gas, a small bubble of it remains in the laboratory vessel under the india-rubber collar attached to the tube *g*, and cannot be expelled. When, therefore, the level of the mercury in the burette is being adjusted, the connection between the burette and laboratory vessel must be left open, and the adjustment be made by working the two reservoirs conjointly. To transfer in the first instance the gases into the burette from the laboratory vessel, the reservoir of the former is lowered, and that of the latter raised, until nearly all the gas has passed over, a little, however, still remaining in the laboratory vessel. The operator at this point must observe whether the gases will require to be compressed or expanded, in order that the mercury in the burette shall stand after final adjustment, at the level of the division line selected for measurement, and in order that, at the same time, the laboratory vessel shall be completely filled with mercury, with the exception, of course, of the space occupied by the small bubble above referred to. With a little practice, the final adjustment may be effected in a few seconds. An indication that the laboratory vessel has been completely filled may always be obtained by causing the mercury or water, if the vessel be moist, to rise to a definite height in the capillary tube *g*.

When the necessary adjustments have been made, the height of the mercury in the pressure tube is read off; the difference between the reading and the number corresponding to the height of the division at which the measurement is made, gives the pressure exerted on the gas in millimetres. The temperature of the water in the cylinder, *c*, is at the same time observed.

The analysis of the gases is conducted in a manner that

is now commonly adopted with this class of apparatus. To absorb the carbon dioxide, a few drops of a strong solution of potash are introduced into the laboratory vessel thus:—The stop-cock of the burette is closed, the reservoir of the laboratory vessel is fixed above the level of the reagent tube, and a small pipette containing the solution of potash is connected with the india-rubber tube attached to the reagent tube. As the reservoir is above the level of the reagent tube, on unscrewing the Bunsen clamp, there will be a tendency for the mercury to flow into the small pipette; and this may be taken advantage of in order to expel the air that collects in the open end of the india-rubber tube to which the pipette is attached. The air having been completely expelled, the reservoir is dropped to a level slightly below that of the reagent tube, and after a few drops of potash solution have been drawn into the laboratory vessel, the Bunsen clamp is screwed up again. The stop-cock may now be opened, and the gas passed from the burette into the vessel. After about ten minutes the carbon dioxide may be considered to have been completely absorbed, and the remaining gases may be transferred to the burette, and again measured, after the mercury has been again adjusted to the levels as before. The remainder of the analysis needs no further description.

When commencing to experiment with the apparatus, it was anticipated that a correction for the error introduced by the bubble of gas being retained in the laboratory vessel, as above described, would be necessary when calculating the volume of the gas. In order to determine the amount of this error, my friend Mr. James Carson very kindly made a number of experiments with the apparatus for me. About 175 c.c. of air were drawn into the burette through the tube *h*, the stop-cock was closed, and the air was compressed until the level of the mercury in the burette reached the 100 c.c. division. The pressure exerted by the air was then found to be equal to 410 m.m. of mercury plus that of the atmosphere, viz., 759.51, that is a total pressure of 1169.51 m.m. of mercury. The air was then passed into the laboratory vessel and back again, the mercury being returned to the same level in the burette; the pressure was read, and found to be exactly the same as before, viz., 1169.51 m.m. The experiment was repeated, and a like result obtained. It was then decided to try a similar experiment with a small volume of air under reduced pressure. About 3 c.c. of air was drawn into the burette, as before, the stop-cock closed, and the volume expanded until the mercury reached the level of the 14 c.c. division line. The pressure of mercury then indicated by the pressure tube was equal to 161 m.m. of mercury; on passing the air into the laboratory vessel, and back again, and adjusting the mercury to the same level as before, the difference of pressure indicated by the pressure tube was found to be less than 0.1 m.m. It is hence evident that the bubble of gas retained in the laboratory vessel is too small to introduce any appreciable error when the adjustments of the levels of the mercury in the burette and laboratory vessel are made, before making measurements, in the manner above described.

(To be continued).

NOTICES OF BOOKS.

Air Analysis: A Practical Treatise on the Examination of Air. With an Appendix on Illuminating Gas. By J. ALFRED WANKLYN and W. J. COOPER. London: Kegan Paul, Trench, Trübner, and Co., Limited.

The manual before us is not, as it will at once appear, a treatise on gas analysis from a technical point of view, but a guide to the sanitary examination of atmospheric air. Of course the processes here taught have their due place in technical gas analysis. The apparatus recommended by Mr. Wanklyn is that of Hempel, which is shown in use

in nine plates. For the determination of oxygen in gaseous mixtures nitric oxide, as used by Priestley and Cavendish, is recommended in preference to the pyrogallic acid process and to combustion with an excess of hydrogen. A reason given is that the two latter methods are inapplicable in presence of carbonic acid. The author distinguishes two methods for the investigation of gases. In the former, to which the name eudiometry is here restricted, a change in the volume of the gas is directly observed. In the second method, which is here named "complementary eudiometry," the analyst notes the action of the gas in question on substances with which it is brought in contact.

This work is calculated to render more general the understanding and the practice of gas analysis, a department which, until lately, has been much neglected.

Electro-Chemical Analysis. By EDGAR F. SMITH, Professor of Analytical Chemistry, University of Pennsylvania. Philadelphia: Blakiston, Son, and Co.

A MANUAL of electrolytic analysis is becoming more and more necessary, as most analytical manuals, from whatever reason, have ignored the subject. At the same time the great advantages of this method in inorganic determinations render a knowledge of its conditions and its resources of great importance to the student and to the practising analyst.

The author, in supplying the want of a systematic exposition of the electrolytic method of analysis is, therefore, conferring a decided benefit upon chemists. He does not exaggerate when he tells us that the electrolytic method of analysis is especially inviting, since it permits of clean, accurate, and rapid determinations where ordinary methods yield unsatisfactory results. He first considers the action of the electric current upon acids and salts. Next he proceeds to a definition of the terms ohm, volt, and ampère, followed by instructions on the sources of the electric current. Here he describes the bichromate cell, the Leclanché, the Daniell with its modifications, the Meidinger, and the "crowfoot," with the Bunsen and the Grove for cases where a current of greater electromotive force is required. Both these cells, he remarks, require constant attention. To thermopiles he objects on the score of their fragility and of the frequent insufficiency of their currents.

As the best source of electric energy for analytical purposes the author recommends secondary batteries of the Julien type. We find next an account of resistances for the reduction of the current down to any required strength, and of the voltmeters and ammeters for measuring currents.

In a survey of the history of the electric method of analysis we find it mentioned that Gaultier de Claubry (1850) was probably the first who applied the current to the detection of metals in solution.

The author then proceeds to the electrolytic determination of the different metals, copper, cadmium, mercury, bismuth, lead, silver, zinc, manganese, iron, uranium, thallium, platinum, palladium, molybdenum, gold, tin, and antimony. The processes for the electrolytic determination of vanadium, tungsten, and osmium are not inserted, as they require further elaboration. A successful method for the electro-deposition of arsenic is not known.

Next we come to the separation of the metals. As regards iron, manganese, zinc, nickel, cobalt, aluminium, chrome and phosphoric acid the methods to be adopted require further elaboration.

Finally come some instructions for oxidations by means of the electric current.

The greatest advantage of the electrolytic method of analysis is its simplicity. We do not require to introduce materials, the purity of which often leaves something to be desired, and which have to be again removed, frequently at the cost of much time and trouble. Hence, where avail-

able, the electrolytic methods of analysis possess an indisputable advantage. We hope that Prof. E. Smith's little work will call increased attention to this branch of mineral analysis.

Sap: Does it Rise from the Roots? Experiments and Observations on Trees and other Plants. By J. A. REEVES. London: G. Kenning.

THE author of this work propounds a novel theory in vegetable physiology. He holds that the sap of plants does not ascend from the roots, but "is obtained by the foliage from the moisture in the air, and from the rain, and more especially from the dews at night, the latter being more frequent and lasting than rain." He tells us that the gas evolved from stable yard manure is found to be superior to that from artificial manures, and is more lasting in its action. Now ammonia is, or may be, given off both from farm-yard manure and from some kinds of artificial manures. But from other very efficient artificial manures, e.g., phosphates and potassium salts, no gases are known to be given off. If Mr. Reeves can demonstrate the existence of a gas given off, e.g., by basic slag, or by "precipitated phosphate" capable of supplying growing crops with their necessary supply of phosphoric acid, he will have done chemists a service which they will appreciate. If, meantime, he wishes it to be understood that farm yard manure, or stable dung, is superior to artificial manures, he is running in the teeth of facts. We should advise him to study experimentally the work of M. Georges Ville.

Wattles and Wattle Barks: Being Hints on the Conservation and Cultivation of Wattles, together with Particulars of Their Value. By J. H. MAIDEN, F.L.S., F.C.S., &c., Curator of the Technological Museum, Sydney. Sydney: Potter.

"WATTLES" is the colonial name for certain species of *Acacia*, rich in tannin and becoming of increasing value in the tanning and, we presume, in the dyeing industries. Contrary to what is now very generally the case in commerce, the demand for these barks, as, indeed, for every drug containing available tannin, is gaining ground on the supply. These trees are able to grow in the poorest soils, and require but little rainfall. Hence they are capable of yielding good returns in districts which would otherwise be deserts. Their systematic cultivation has been already undertaken with success in the Colonies of Victoria and South Australia, and it is now recommended for New South Wales.

Of the 312 (*sic*!) Australian species of *Acacia* not all are equally valuable. One of the finest is the *Acacia mollissima*, called indiscriminately by the colonists "black wattle," "green wattle," and "silver wattle." The bark, according to Baron Mueller (*Extra-Tropical Plants*), yields in the dry state from 30 to 54 per cent of tannin. 1½ lbs. of black wattle bark give 1 lb. of leather, whereas 5 lbs. of English oak-bark are required for the same quantity. A quarter and even half a ton of bark is sometimes obtained from a single tree. The bark of *Acacia pycnantha*, the "broad-leaved wattle," yields up to 46.47 per cent of tannin in South Australia.

The preparation of extracts of these naturally arises, and it has, in fact, been successfully attempted at Echunga, in South Australia. It was, however, complained that the extracts were undesirably rich in gum, and that a part of the tannin was destroyed during the process of concentration. These difficulties, however, could doubtless be overcome.

Would it be possible to use these barks as a source of tannic acid?

Concerning the adaptability of the wattle barks for the purposes of the dyer and the tissue-printer we find no data.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—As you have opened your columns to correspondence on this subject, I should like to take this opportunity of observing that in the main I cordially agree with the views propounded in your last issue by Mr. Arnold Philip.

It appears to me that the Chemical Society is intended to be an association or club, as it were, formed by persons interested in the progress of chemical science, and that any one who is thus interested has a reasonable claim to membership, whether he be a professional consultant or analyst, a scientific investigator, a manufacturer, a teacher, or simply an educated individual with scientific proclivities. No qualification of any kind beyond the possession of such an interest appears to me to be indispensable for membership; and by insisting on qualifications based on having conducted researches, or holding teaching appointments, &c., &c., a grave injustice would be done to many who have sufficient knowledge of chemical science to wish to belong to an association formed to further the pursuit of that branch of knowledge, but have not pushed their studies sufficiently far to entitle them to put forward such qualifications.

Further, the notion of endeavouring to some extent to imitate the Royal Society by making critical selections of candidates would, I imagine, be in the long run extremely prejudicial to the interests of the Society. The number of persons annually admitted would materially diminish, and in consequence the maintenance of the excellent *Journal of the Society* would be jeopardised if not rendered impracticable, at least in its present form.

On the other hand, it is unfortunately the fact that certain persons have obtained admission to the Society who use the letters F.C.S. in an objectionable way for advertising purposes; also that the bulk of the general public are still so densely ignorant of almost everything pertaining to science, that the employment of these initials is often taken to be a sort of guarantee that the person using them is necessarily skilled in all sorts of professional matters.

The proper remedy for the first of these evils is, I conceive, that the Society should acquire powers to prevent anyone from using the letters F.C.S. unless he actually at the time belongs thereto, and to expel and deprive of membership anyone misusing his privileges as a Fellow. Probably this is impracticable under the present charter; if so, it is worth considering whether it would not be well to resign it and obtain another conferring the requisite powers.

As regards enlightening the general public in reference to the wide difference subsisting between societies instituted for the advancement of abstract science (such as the Chemical, Linnean, &c.), and qualifying bodies dealing with the professional applications of science (such as the Royal Colleges of Physicians and Surgeons, the Institute of Chemistry, &c.), it is to be hoped that in time the general progress of education will enable such distinctions to be more widely appreciated than is the case at present. It seems to me, however, that the qualifying bodies, rather than the purely scientific ones, are the proper agents to take active steps in the direction of instructing the public in such matters; and that as regards the particular points raised by Drs. Teed and Lloyd, what is chiefly wanted is that the Institute of Chemistry should

be roused up from the lethargy to which it has apparently fallen a prey of late years.—I am, &c.,

C. R. ALDER WRIGHT.

Chemical Laboratory,
St. Mary's Hospital Medical School, London, W.C.,
October 12, 1890.

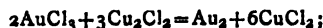
RAPID DETERMINATION OF TIN IN MINERALS.

To the Editor of the Chemical News.

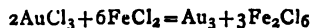
SIR,—In the *CHEMICAL NEWS*, vol. lx., p. 271, there is an article entitled "A New, Easy, Rapid, and Correct Method of Detecting Tin in Minerals," by Alexander Johnstone, F.G.S. The method therein described for obtaining the beads of metallic tin is substantially that known as "Gahn's method." But to prove that the beads so obtained are tin, Mr. Johnstone recommends that "two or three drops of boiling concentrated hydrochloric acid be poured over them in the mortar; and then, by means of a glass tube, one drop of a fairly strong solution of gold chloride be mixed with the hydrochloric acid solution." "Then," he adds, "if the white metallic scales originally observed were composed wholly or partly of tin . . . the bottom of the mortar will receive a distinct purple stain by the formation of the well-known characteristic purple of cassius; also further confirm the presence of tin by allowing a current of SH_2 gas to impinge for a short time on the moist stained bottom of the mortar, &c."

Now, as several other metals besides tin may be obtained by "Gahn's method," and as some of these would give substantially the same reactions as tin, when treated as directed by Mr. Johnstone, it may be well to caution the unwary chemist or mineralogist not to place implicit confidence in what might seem a positive indication of the presence of tin from the use of the above tests.

As a matter of fact, the blowpipe tests for tin are very unsatisfactory, save in such minerals as contain a high percentage of the metal unmixed with other easily reducible metals. I was forcibly reminded recently of the danger of depending too much upon what seemed to be a positive indication of tin in a certain complex ore. I had followed the directions of Mr. Johnstone carefully in the above-referred to test, and obtained what seemed to be positive indications of the presence of tin, when, upon reflection, it occurred to me that some other metal or metals might be present instead, and upon further examination I found that tin was entirely absent, and that the only metal present, in appreciable quantity, were lead and copper. The action of HCl on Cu in the presence of air had produced cuprous chloride, and the following reaction took place on the addition of AuCl_3 :—



but in consequence of the resemblance between thin laminæ of iron and tin (this metal with spangles of lead mixed) would be more liable to mislead than Cu , by the formation of ferrous chloride, which would reduce the AuCl_3 , as follows :—



To adopt this otherwise convenient method for the detection of tin in minerals to such cases as it now evidently is unsuited, I would suggest the removal of the interfering metals (previous to fusion) by means of (NO_2HO) nitric acid.—I am, &c.,

THOMAS CHARLTON.

Rocky Mountain Smelting Co.,
West Cliff, Colorado,
September 23, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 12, September 22, 1890.

Account of a Scientific Ascent of Mont Blanc.—J. Janssen.—The author's object was to solve the controversial question of the presence of oxygen in the solar atmosphere. At the end of October, 1888, he had ascended Mont Blanc up to the hut of the Grand Mulets, situate at the altitude of 3000 metres, above the junction of two of the glaciers which descend from the north slope of the mountain into the valley of Chamounix, *i.e.*, those of Bossons and of Tacconoz. The observations then made showed, in the rays due to the action of the atmospheric oxygen, a decrease proportionate to the height of the station, and which indicated that at the limits of our atmosphere these groups would disappear entirely, and that, consequently, the solar atmosphere did not intervene in the production of the phenomena. The decrease of intensity of the group B between the Grand Mulets and the station of the Bosson, near the summit, was surprising, being greater than seemed to result from the height and the density of the atmospheric column between the two stations. The totality of the author's observations compel us to recognise the absence of oxygen in the gaseous solar coatings which surmount the photosphere; at least, oxygen with the constitution which enables it to exert upon light the phenomena of absorption which it produces in our atmosphere, and which are manifest in the solar spectrum by the system of rays and bands which we know. It is certain that if oxygen exists simultaneously with hydrogen in the exterior envelopes of the sun, and accompanies the latter element to the coronal atmosphere, the ultimate refrigeration at a period of time which we cannot yet fix would have the effect of provoking the combination of oxygen and hydrogen if jointly present. Watery vapour would then be formed in these gaseous envelopes, and the presence of such vapour, according to what we know of its properties, would oppose a considerable obstacle to the solar radiations, especially those which produce heat.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 11.

Action of Oxygenated Water upon the Oxygen Compounds of Manganese.—A. Gorgeu.—In this second memoir the author examines, at considerable length, the action of oxygenated water upon permanganic acid and the permanganates.

Action of Oxygenated Water upon Hydrated Manganese Oxide.—A. Gorgeu.—The author, in opposition to M. Carnot, maintains that this reaction, in the varied conditions under which he operated, always obtained a compound bordering on the sesquioxide and containing 10·10 per cent of oxygen.

On the Selenium Chlorides.—W. Ramsay, F.R.S.—The author upholds the accuracy of his former communication as against M. Chabré. He submits that a body which, even in presence of an excess of selenium, distils with dissociation between 130° and 170° cannot boil about 300° without decomposition.

On the Dissociation of Selenium Chloride.—W. Ramsay, F.R.S.—A supplement to the last communication. The author considers that M. Chabré was in error in submitting the sub-chloride to distillation. The boiling-point does not exceed 190°, even when the temperature of

Manufacture of Colourless Tannins.—A. Villon.—See p. 195.

the oil-bath is 300°. The conditions are very different when its vapour is exposed to a temperature of 300°. He believes that it is then completely dissociated.

On the Oxidising and Decolourising Properties of Carbons.—P. Cazeneuve.—It results that if the decolourising properties of charcoal are due to a mechanical fixation of the colours upon the carbonised matter, we must not neglect the part played by the oxygen condensed in the pores in a state comparable to ozone, and exerting an evident destructive action upon certain colours, and, on the contrary, occasioning the production of certain other colours, which are oxidation products.

On the Conditions of Equilibrium of Saturated Carbon Compounds.—J. A. Le Bel.—This paper does not admit of useful abstraction.

A Characteristic Reaction of Hydrogen Peroxide.—G. Denigès.—If a solution of 10 per cent of ammonium molybdate in water is mixed with an equal volume of concentrated sulphuric acid (say 1 c.c. of each) it gives, with a few drops of oxygenated water, a decided yellow colour, equal in intensity to the solutions of the alkaline chromates and di-chromates.

On Paranitro-ortho-toluene sulphonic Acid.—J. Hauser.—The sulpho-conjugated acid of paranitro-toluene displaces sulphuric acid in soluble sulphates. Metasulphonated nitrotoluene seems to possess the same properties as its isomers.

Revue Générale des Sciences Pures et Appliquées.
Vol. i., No. 16, August 30, 1890.

The Chlorides of the Bibasic Acids.—Victor Anger.—The only acids which can form dyssymmetric chlorides are those in which the carboxyls are in the position 7, or, as it is otherwise called, in the position 1·4. Here there is a manifest approximation to the production of the lactones and the lactames.

Vol. i., No. 17.

Researches on the Absorption of the Ultra-violet Rays of Various Substances.—J. Soret and A. Rillet.—The authors commenced investigations on this subject about ten years ago, and have latterly been chiefly engaged with bodies of the fatty series. They have encountered considerable difficulty in obtaining these bodies in a state of purity, which interferes with the accuracy of the results. The alcohols present a high transparency. Rectification and especially complete desiccation occasion a decomposition or an oxidation of the alcohols, which often diminishes their transparency. It would be premature to affirm that there exists a determined difference of transparency among the various alcohols if perfectly pure. The authors cannot, therefore, confirm the conclusion of Hartley and Huntington, that the transparency of alcohols diminishes progressively as their chemical formula becomes more complicated. The measure of absorption of the ultra-violet rays constitutes a very delicate means for appreciating the purity of alcohols. Aldehyd, if undiluted, intercepts the ultra violet rays almost completely. The acetones are very absorbent. The energetic absorption of aldehyd and the acetones is probably due to the group carbonyl, CO, for if this group is replaced by O we obtain very transparent bodies. The authors have finally made summary researches on the absorption of the ultra-violet rays by the vapours of different organic substances, and have been able to demonstrate that very opaque liquids, if sufficiently volatile, give vapours which exert a sensible absorption.

FOR SALE.—THE CHEMICAL GAZETTE.
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THE CHEMICAL NEWS.

VOL. LXII. No. 1613.

ON THE INFLUENCE OF HEAT ON COPPER-POTASSIUM CHLORIDE AND ITS SATURATED SOLUTION.*

By Prof. VAN 'T HOFF.

THE blue crystals of copper-potassium chloride,—



when heated upwards to 100° change their colour, and more close investigation proves such is due to the formation of a new brown salt, $\text{CuCl}_2 \cdot \text{KCl}$, according to the equation $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O} = \text{CuCl}_2 \cdot \text{KCl} + \text{KCl} + 2\text{H}_2\text{O}$.

This same new substance can be obtained at low temperatures, on heating the blue double salt in presence of copper chloride; it then results from a reaction, given by the following symbols:—



Both these transformations are reversible, *i.e.*, the primitive substances are obtained anew on cooling, and both take place at definite temperatures, 93° and 56° respectively, which temperatures can be accurately determined in studying the abrupt change of volume which accompanies that of chemical composition.

The temperatures of 56° and 93° are, moreover, characterised by an interaction of three curves of solubility, in each case, *viz.*:—

1. At 56° the following three will meet:—

- That of the system $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}, \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.
- That of the system $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}, \text{CuCl}_2 \cdot \text{KCl}$.
- That of the system $\text{CuCl}_2 \cdot \text{KCl}, \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

2. At 93°:—

- That of the system $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}, \text{CuCl}_2 \cdot \text{KCl}$.
- That of the system $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}, \text{CuCl}_2 \cdot \text{KCl}$.
- That of the system $\text{CuCl}_2 \cdot \text{KCl}, \text{KCl}$.

Lastly, those same temperatures are characterised also by an intersection of four vapour pressure curves at each, *viz.*:—

1. At 56° those of the above-mentioned three saturated solutions and that of the dry blue salt, mixed with copper chloride, meet.

2. At 93° those of the other three mentioned above and that of the dry blue salt mixed with potassium chloride.

Amsterdam, Sept. 14, 1890.

THE ESTIMATION OF NITRITES IN POTABLE WATERS.†

By JOHN C. THRESH, M.B., D.S.C.,
Medical Officer of Health.

PROBABLY no analyst feels that he has made a complete examination of a water unless he has at least made a qualitative test for nitrites, and if he finds indications of their presence he justly regards the water with suspicion, but, uncertain what further inference to draw, a quantitative examination is rarely made. Though this quantitative analysis, therefore, does not seem to be a matter of much importance in the present state of our knowledge, a series

of experiments I am now making on the changes in composition of certain waters, by keeping under varied conditions, lead me to believe that ere long the study of these changes will be of great aid in enabling us to judge of the quality of a water, and especially of those waters which at the present time the chemist or medical officer can only state to be suspicious. One of these changes, and one of the most easily followed, is the variation in amount of nitrous nitrogen. As an example I will quote that of the most extreme case I have yet met with. A water which from a mere chemical analysis would have been passed as "usable" when examined soon after drawing from the pump showed no trace of nitrites. Three days after it contained no less than 3·5 parts of nitrous nitrogen per litre, and on the sixth day after, it was again free from nitrites. Other changes proceeded *pari passu*, and these together with a bacteriological examination proved the water to be seriously contaminated.

It was when commencing this investigation that the want of a simple and reliable quantitative test for nitrites made itself felt. The metaphenylene-diamine and the naphthylamine tests were fairly tried, but did not answer my purpose, neither did titration with potassium permanganate. In working out the process for determining the amount of dissolved oxygen in water which I described early this year in a paper read before the Chemical Society, the action of nitrous acid on potassium iodide in the presence of a varying proportion of free oxygen was determined, and the results led me to believe that after all the old potassium iodide and starch test for nitrites could be made a reliable colorimetric quantitative one for water analysis. The results of my experiments having this for their object may be summarised as follows:—

1. With the same proportions of acid, starch, and potassium iodide, the rapidity with which the blue tint is developed, and the depth of tint varies with the degree of oxygenation of the water.

2. The depth of tint increases with the time which elapses between the addition of the reagents and the observation. This is due to the fact that the NO liberated is acting continuously as a carrying agent between the oxygen dissolved in the water, and of the air in contact with the surface of the fluid and the hydric iodide, liberating an equivalent of iodine corresponding to the oxygen carried.

3. The effect of temperature is such that comparisons cannot be made unless the fluids are within 2° or 3° of the same temperature. Thus, *e.g.*, at 65° F., in very weak solutions, the colour is not developed so rapidly as at 60° F., *ceteris paribus*.

4. With the same proportions of starch and iodide and in samples fully oxygenated, &c., the colouration varies with the amount and nature of the acid used.

5. The amount of potassium iodide added affects the result considerably. The larger the proportion of iodide, within certain limits, the greater the rapidity of the reaction.

6. The quantity and nature of the starch solution are also factors requiring recognition. If too large a proportion of starch be added, a marked reddish tint is first developed instead of the blue tint, and this reaction is still more marked if the starch solution has begun to change by keeping.

7. When all the above factors are constant, then the rapidity with which the blue tint is developed and the depth of tint varies directly with the amount of nitrite present in the water.

I need not trouble you with the account of the numerous experiments upon which these conclusions are based, nor of the further investigation conducted to ascertain how the information so obtained could be made available for rendering the iodine and starch reaction reliable as a quantitative test. I will merely give you now an account of the reagents required and the mode of conducting the analysis which I have found to give the most satisfactory results.

* Abstract of a Paper read before the British Association, Leeds Meeting, 1890, Section B.

† From the *Pharmaceutical Journal*, September 20, 1890.

Reagents:—

1. *Solution of Starch and Potassium Iodide.*

Starch in powder	0.2 grm.
Caustic potash	1.0 "
Potassium iodide	2.0 grms.
Water	200 c.c.

Add the starch to 10 c.c. of water, and when uniformly diffused add the caustic potash. Dissolve without the aid of heat and add the remainder of the water and the potassium iodide. Strain or filter. This solution keeps for months without appreciable change. One c.c. is required for each determination.

2. *Dilute Sulphuric Acid.*

Pure sulphuric acid	1 vol.
Distilled water	3 vols.

This is the same strength as used for the permanganate test, and I always employ it for both purposes.

3. *Solution of Sodium Nitrite.*

Sodium nitrite	0.493 grm.
Water	1 litre.

Dissolve:—

1 c.c. = 0.1 m.gr. nitrogen.

Apparatus.—Two or more 50 c.c. Nesslerising cylinders. **Process.**—Shake the sample of water vigorously in a bottle only partially filled, to saturate with air; pour 50 c.c. into the cylinder, and add 1 c.c. of the starch and iodide solution, and afterwards 1 c.c. of the dilute acid. Stir. Assuming the temperature to be about 60° F., if a dark blue tint develops instantaneously the water contains more than 1 per million of nitrous nitrogen. If it becomes blue in a few seconds it contains about 0.1 per million. If it requires more than 10 seconds to develop it contains less than this amount.

If the blue colour appears instantly the water must be diluted with known proportions of nitrite free water (saturated with air) until it is found by experiment that the colour takes a few seconds to develop.

With a very little experience the approximate amount of nitrite present can be ascertained with considerable precision by these simple preliminary experiments. Now prepare a standard solution of sodium nitrite by diluting 1 c.c. of the strong nitrite solution with 200 c.c. of water. One cubic centimetre of this weaker solution diluted to 50 c.c. corresponds to 0.01 m.gr. nitrous nitrogen per litre.

Measure into the Nessler glasses varying quantities of this dilute nitrite solution and fill up with water. Now take 50 c.c. of the water to be examined, or of the diluted water, if dilution were found necessary, and to each add successively 1 c.c. of the starch and iodide solution and dilute acid and note how the blue tint develops. If none of the solutions correspond with the water a fresh series must be prepared. In this way, in a very few minutes the amount of nitrite in any sample of potable water can be easily obtained with a very considerable approach to accuracy.

Since I commenced employing this test I have analysed over 180 samples of water, 51 of which contained nitrites, varying from 0.005 to 3.4 parts nitrogen per million, and I have had no reason to suspect inaccuracy from the interference of other constituents in any single case.

To render the process more intelligible I will give details of two determinations. Two solutions were prepared for me by an assistant and marked "a" and "b" respectively.

a. Fifty c.c. + reagents gave a blue tint in about ten seconds. It was therefore about the proper strength for estimation.

Ten c.c. of the dilute nitrite solution was diluted to 50 c.c. and compared with the sample. The colour seemed to develop a little more rapidly, but the difference was not very marked. Three solutions were prepared by diluting

5, 7, and 9 c.c. respectively of dilute nitrite solution to 50 c.c.

5 c.c. = 0.05 N per million	too weak.
7 c.c. = 0.07 "	"
9 c.c. = 0.09 "	too strong.

Another solution containing 0.08 N per million was then made and compared with the sample; the blue tint developed a little more rapidly. The strength was certified to be 0.075 N per litre. The actual strength was 0.07 per litre.

b. Original water gave a dark blue instantly.

Diluted to 1-10th a pale blue	"
" 1-25th colour developed in a few seconds.	"
Compared 1-25th with 0.05	too weak.
and 0.10	little too strong.

Now compared with:—

0.08	too weak.
0.09	about right.
0.10	too strong.

0.09 + 25 = 2.25 N per litre. The actual strength was said to be 2.5 N per litre.

The following results may also be quoted as fair examples of the accuracy obtainable:—

Nitrous Nitrogen per litre.		
	Present.	Found.
1	0.1 per million	0.10 per million.
2	0.625 "	0.65 "
3	0.625 "	0.625 "
4	0.093 "	0.095 "
5	0.01 "	0.01 "
6	0.05 "	0.05 "
7	0.125 "	0.13 "

The time occupied by a determination is usually about 5 minutes, the reagents are easily made and preserved, and the necessary conditions easily observed. I can, therefore, recommend the process to such as may desire at any time to estimate the nitrites in potable waters.

ON AN APPARATUS APPLICABLE FOR GAS ANALYSIS AND OTHER PURPOSES.*

By W. E. ADENEY, F.I.C., Assoc. R.C.Sc.I.,
Curator and Examiner in Chemistry in the Royal University, Dublin.

(Concluded from p. 199).

THE following results, taken at random, of analyses of sewage and of air will serve to indicate the degree of accuracy which is ordinarily attainable with the apparatus:—

(I.) Analyses of the gases resulting from the combustion of the residue obtained by evaporating 50 c.c. of the sample of sewage with metaphosphoric acid to dryness.

All measurements made at the 14 c.c. division line on the burette. Closed pressure tube employed.

	I. M.m.	II. M.m.
Height of mercury in pressure tube (moist)	776.5	786.0
" " " burette	351.0	351.0
Pressure of the gas	425.5	435.0
Temperature	20° C.	20° C.

After absorption with potassium hydrate:—

Height of mercury in pressure tube	514	512
" " " burette	351	351
Pressure of gas after absorption of CO ₂	163	161
Tension of CO ₂	262.5	274.0

* Read before the Royal Dublin Society, Jun: 18, 1890.

After absorption with pyrogallic acid :—

Height of mercury in pressure tube	509.5	511.0
" " " burette	351.0	351.0
Pressure of nitrogen	158.5	160.0
Capacity of burette at 14 c.c. division line = 14.2267 c.c.		

The parts per 100,000 of organic carbon and total nitrogen contained in sewage are calculated from the above determinations in the ordinary way.

Analysis No. I. gives :—

4.9 parts carbon per 100,000
6.96 parts nitrogen per 100,000

Analysis No. II. gives :—

5.1 parts carbon per 100,000
7.02 parts nitrogen per 100,000

(II.) Analyses of air. About 175 c.c. air at ordinary pressure taken.

All measurements made at the 100 c.c. line on burette. Open pressure tube employed.

	I. M.m.	II. M.m.
Height of mercury in pressure tube	628.50	628.5
Atmospheric pressure	755.75	759.1
Total pressure	= 1384.25	1387.6
Height of mercury in burette	210.00	210.0
Pressure of the gas	= 1174.25	1177.6

After absorption with potassium hydrate :—

Total pressure	1173.45	1176.80
Tension of CO ₂	0.80	0.80

After absorption with pyrogallic acid :—

Total pressure	933.25	936.30
Tension of oxygen	240.20	240.50
Temperature	16.5° C.	18.4° C.
Tension of nitrogen	919.286	920.911
Tension of aqueous vapour at 16.5 = 13.964 m.m.		
" " " " 18.4 = 15.389 m.m.		

	I. M.m.	II. M.m.
Percentage of nitrogen	= 79.2299	79.2379
" oxygen	= 20.7001	20.6933
" carbon dioxide	= 0.0689	0.0683

When explosions are to be made in the apparatus, the gas is first measured as above described; the oxygen or hydrogen is then passed into the laboratory vessel through the reagent tube, and after the mixed gases have been measured, they are returned to the laboratory vessel and exploded therein under reduced pressure according to the directions given by Thomas (*Chem. Soc. Journ.*, xxxv., 213).

The hydrogen or oxygen may be passed into the laboratory vessel with great facility. The gas is first collected in a test-tube or other suitable vessel over mercury; the india-rubber tube attached to the reagent tube is then carefully freed from air and filled with mercury in the manner above described, and cautiously inserted into the test-tube; then, on lowering the reservoir, the gas will pass from the test-tube into the laboratory vessel.

The method of employing the apparatus for the analysis of nitrates or carbonates, and for other similar purposes, will be understood from the foregoing descriptions. It need only be mentioned that a known quantity of the substance to be analysed is placed in a small flask in the solid form or in solution, and the flask is attached to the tube *h* of the apparatus. The flask is exhausted and the necessary reagent added through the cup and stop-cock *g*.

I trust in a future communication to the Society to give the results of a research on certain methods of water analysis upon which I have been engaged for some time past, and to show how the apparatus may be conveniently

employed for determining the dissolved gases, organic carbon, and the nitrogen in waters.

In the early part of this paper it was pointed out that the reservoir supplying mercury to the burette and pressure tube was connected with the latter and not with the former. With this class of apparatus such an arrangement is essential, because, when the reservoir is kept for any length of time at a lower level than that of the bottom of the burette, and this is constantly necessary when working in vacuo or under reduced pressure, air diffuses through the india-rubber connecting tube, and passes into the pressure tube immediately the reservoir is raised again. It would, of course, pass into the burette, and the experiment would be vitiated if the connecting tube were directly attached to the burette. The air may be expelled from the pressure tube when necessary by opening its stop-cock and raising the reservoir sufficiently high to fill the tube with mercury.

It will be noticed that the pressure tube is not provided, as in the case of Thomas's or Macleod's apparatus, with a water jacket for keeping its contents, when employed as a closed and "wet" pressure tube, at the same temperature as the contents of the burette, nor are means furnished for continually renewing the water in the cylinder *c* during an analysis. I have found that neither additions are necessary to this class of apparatus for all ordinary purposes. Since the burette is of a considerable length, viz., 640 m.m., the measurements may in nearly all cases be made with advantage with an open pressure tube; and if the cylinder *c* be filled with water that has been kept exposed for some time to the temperature of the laboratory in which the apparatus is kept, the water will not, if ordinary care be observed, alter sufficiently to appreciably affect the results of an analysis. When it is necessary to use a closed pressure tube, and it is at the same time necessary to work with the utmost degree of accuracy, then it is preferable to employ a "dry" closed tube; but even if it be employed "wet" very good results will be obtained. The additions above referred to have the great disadvantage of rendering the apparatus much more complicated and liable to fracture. I have endeavoured to make the apparatus here described as simple as proper regard for accuracy of result will allow, in the hope that it will supply the want of an effective and simple apparatus, which I have, in common with other chemists, experienced in teaching methods of analysis involving the evolution, collection, and measurement of gases, and that it will be consequently found useful in a laboratory in which advanced students are taught, as well as for the purposes of research work.

With reference to the possibility of maintaining the apparatus in good working order, I may say that I have employed it for a large number of experiments of various kinds during the past six months, and have found no difficulty in maintaining the stop-cocks in such good order that a vacuum can be maintained in the burette and pressure tube unimpaired for several days. Some difficulty was at first experienced when attempting to subject a gas in the burette to high pressure, owing to the stopper of the burette being loosened and pressed out. The difficulty was overcome by lubricating the stopper with a mixture of beeswax and vaseline.

Other advantages of the apparatus besides simplicity and wide range of applicability are its comparative freedom from the risk of breakage, and its cheapness. The glass parts,* with the exception of the scale at the back of the pressure tube, were obtained at a cost of 45s.; the cost of putting the parts together, including time and fittings, was about 40s.; and it may be taken that the apparatus cost in all not more than £5.

In conclusion, I desire to express my sincere thanks to my old pupil and friend, Mr. James Carson, C.E., Assoc.

* My acknowledgments are due to Messrs. Baird and Tatlock, of Glasgow, through whom I obtained the glass parts of the apparatus, for the care and accuracy with which all the directions given to them were carried out.

R.C.Sc.I., for the aid he has unsparingly given me in making a large number of laborious experiments with which to test the apparatus. My thanks are also due to John Connolly, the laboratory assistant in the Royal University, for the skilful assistance he has rendered me in fitting the apparatus together.

THE OXIDATION OF SULPHIDES BY MEANS OF THE ELECTRIC CURRENT.*

By EDGAR F. SMITH.

IN the *Proceedings* of the Chemical Section of the Franklin Institute, i., 52, and the *Berichte*, xxii., 1019, a preliminary report was published, describing a rapid method for the conversion of sulphur into sulphuric acid through the agency of the electric current. It was there demonstrated that the sulphur in the mineral chalcopyrite, for example, was completely oxidised to sulphuric acid in ten minutes, and that the oxides Fe_2O_3 , CuO , &c., were eliminated from the analysis, so that the barium sulphate finally weighed was perfectly white in appearance, and not contaminated with the impurities usually accompanying it when precipitated from solutions containing much iron, &c.

To give a better idea of the mode of carrying out an oxidation of this description, the apparatus used for this purpose will be first outlined.

T represents a table upon which stands *A*, an ordinary filter-stand, in the base of which is fixed a binding screw holding in position a heavy copper wire bent as seen in the sketch, and intended to carry the nickel crucible in which the oxidation occurs. The arm of the filter-stand has attached to it a binding screw holding a heavy platinum wire, as well as the copper wire generally in connection with the anode of the battery. *E* is a Kohlrausch ampere-meter, registering amperes and half amperes; this is in connection with *C*, a block of wood screwed or nailed to the table. There are four depressions (*x*) in *C* containing a few drops of mercury, in contact with the binding screws (*a*). *D* is the movable top of *C*; the wires crossing it project on the under side and rest in the mercury cups (*x*). When *D* is so arranged that the wires on its upper face run in the direction of the dart, the crucible becomes the anode of the battery, whereas if they have a horizontal position, —→ the crucible is the cathode.

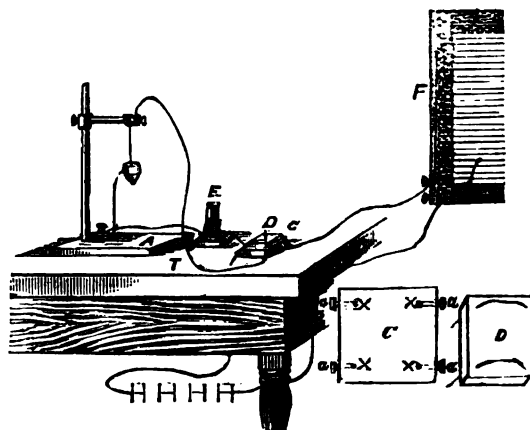
F is a resistance frame, consisting of about 500 feet of common iron wire arranged upon a light wooden parallelogram. It should always be in the circuit.

The movable cap *D* is necessary and important. It enables the operator to change the poles quickly—to reverse the current at a moment's notice. In the oxidations to be described later on, this was frequently necessary, chiefly because when the crucible served as cathode in many of the decompositions there often occurred a considerable deposition of metal upon its sides, and in the act of separating this metal enclosed undecomposed material and withdrew it from the field of oxidation. In such cases, by making the crucible the anode, as above indicated, the mineral matter will be liberated, and, upon coming in contact with a large oxidising surface, all the sulphur contained in it will be converted into sulphuric acid. The crucible should always be covered during the oxidation.

Oxidation of the Sulphur in Sulphides.

In the oxidations given later, nickel crucibles $1\frac{1}{2}$ inches high and $1\frac{1}{2}$ inches wide were used; but a more advantageous form, one which should always be employed when more than 0.15 gram of material is used, would measure

2 inches in length and $1\frac{1}{2}$ inches in width. In such a vessel place 25–30 grms. of pure potassium hydroxide (not sodium hydroxide), and warm the same until the excess of moisture is expelled. Bring the weighed sulphide into the crucible, connect the latter with the copper wire shown in the sketch, and lower the platinum wire so that it extends a short distance below the surface of the molten mass. The current is then made to pass by bringing a metallic cup, connected with one pole of the battery, in contact with one of the wires of the resistance frame, *F*. The sulphur will be completely oxidised in from ten to twenty minutes. Interrupt the current, allow the crucible and contents to cool, then place the same in water. In a few minutes all but the insoluble oxides will have dissolved. Filter, acidulate the warm filtrate with hydrochloric acid, and precipitate the sulphuric acid in the usual manner. If, upon adding acid to the alkaline solution the latter becomes turbid, from separated sulphur, it is an indication that the oxidation was incomplete. Observe closely whether sulphur dioxide is liberated even when the liquid remains clear. Never omit the examination of the residue remaining on the filter, after the alkaline solution has been filtered. The caustic alkali must always be tested for sulphur before using it in this work. It is well to estimate the impurities in the alkali and deduct them, in each determination, from the barium sulphate found.



To ascertain to what extent this method could be applied in oxidising sulphur, the following minerals, representing all the various classes of natural sulphides, were subjected to experiment:

Sphalerite (ZnS).

No difficulty was experienced in oxidising the sulphur of this mineral. A current of one ampère (=10.45 c.c. electrolytic gas per minute) was amply sufficient for the purpose. When the mineral was added to the melted caustic potash and the current applied, the mass assumed a muddy appearance, which it retained for ten minutes, when it became white and froth-like. It was discovered, by experiment, that this appearance indicated the complete oxidation of the sulphur.

(I.) 0.1195 gram. mineral, 20 grms. alkali, 1 ampère (time, 20 minutes), gave 32.97 per cent S.

(II.) 0.1025 gram. mineral, 20 grms. alkali, 1 ampère (time, 20 minutes), gave 32.96 per cent S.

(III.) 0.1180 gram. mineral, 20 grms. alkali, 1 ampère (time, 10 minutes), gave 32.80 per cent S.

By oxidising the sulphur in a fourth portion with nitric acid and potassium chlorate, 32.90 per cent sulphur was obtained.

A specimen of Joplin (Mo.) blende gave 32.60 per cent and 32.80 per cent S by the nitric acid method, while by the electrolytic method 32.90 per cent S was found.

* Read at the Chemical Section of the Franklin Institute, June 17, 1890.

An impure sphalerite, locality unknown, in which there was considerable gangue and other admixtures, gave 29·8 per cent S when oxidised with nitric acid, and when acted upon in alkaline solution by a current giving one ampère of electrolytic gas per minute, the sulphur found was :

(I.)	29·23	per cent S.
(II.)	29·45	" "
(III.)	29·68	" "
(IV.)	29·67	" "
(V.)	29·90	" "
(VI.)	29·58	" "

Cinnabar (HgS).

Very pure material was employed in this oxidation. Several trials were required, in order to learn the proper conditions for successful working. The tendency of this mineral, when finely divided, was to collect in lumps, which appeared to rise and fall in the alkaline solution; in order to bring every particle of material within the field of oxidation, the current was reversed every few minutes. By doing this the sulphur was completely oxidised in twenty minutes or even in less time. If the precaution just mentioned with reference to the reversal of the current be not heeded more time will be required for complete oxidation, and even then it will be doubtful whether the sulphur is fully converted into sulphuric acid. Twenty-five grms. of caustic alkali were used in each experiment with this mineral.

0·1089 grm. cinnabar gave 13·82 per cent S, while the required percentage is 13·79.

A current of two ampères per minute was used.

Galenite (PbS).

There is no difficulty in oxidising this mineral. The same quantity of alkali and the same current strength were employed here as in the mineral immediately preceding :

(I.)	0·1093	grm. galenite	gave	14·30	per cent S.
(II.)	0·1092	" "	" "	14·60	" "

Another portion in which the sulphur was oxidised by heating the mineral in a current of chlorine gave 14·30 per cent S.

Argentite (Ag₂S).

No difficulty was encountered in oxidising this mineral. The decomposition was made with conditions analogous to those already described. Silver did not pass into the alkaline solution, so that when the sulphuric acid was precipitated, barium chloride was employed as usual. The specimen analysed being exceedingly pure, it was not thought necessary to determine the sulphur by any other method. None of it remained unoxidised :

0·1032 grm. argentite gave 13·04 per cent S; required 12·90 per cent S.

Chalcocite (Cu₂S).

Thus far this mineral has resisted all efforts to convert its sulphur into sulphuric acid. Repeated attempts have been made, but not more than half of the sulphur contained in the mineral was oxidised, notwithstanding the current was very much increased in each trial. Since some time may elapse before another opportunity offers itself to continue experimentation with this mineral, it need only be stated that a modification of the usual method will be tried upon it. The copper and sulphur are evidently in very intimate union.

Molybdenite (MoS₂).

The sulphur in this mineral is given up readily to the oxidising influence of the current. One annoying feature is that the fine mineral particles are so very light that they are apt to be carried up and adhere to the cover crystal. In this oxidation the poles should be repeatedly reversed. The result given below is from a sample that contained much quartz, &c. The residue, however, gave not a trace of sulphur when tested for it.

0·1045 grm. mineral gave 0·2785 BaSO₄ = 36·60 per cent S.

Stibnite (Sb₂S₃).

While a current of two ampères was employed in this oxidation, the sulphur can be completely changed to sulphuric acid with one ampère. Three trials proved this conclusively.

0·1095 grm. mineral gave 0·2230 BaSO₄ = 27·91 per cent S; required sulphur, 28·5 per cent.

Orpiment (As₂S₃).

Pure material could not be obtained, so that the experiments were made with inferior mineral, and the greatest care was given the oxidation, so that sulphur was not afterwards discovered in the insoluble residue.

0·1150	grm. sub.	gave	0·2922	gr. BaSO ₄	=	34·90	p.c. S.
0·1044	" "	" "	0·2721	" "	=	35·79	" "

The arsenic was also oxidised to arsenic acid. Several tests proved the conversion to be quantitative. Results obtained in this direction will be published later.

Jamesonite (Sb₂S₅Pb₂).

The sulphides of lead and antimony offer no difficulty in the oxidation of their sulphur. This sulpho-salt is decomposed with equal facility. A current of two ampères per minute was employed. The crucible was the anode for ten minutes, and the cathode for an equal period.

(I.) 0·1078 grm. mineral gave 0·1426 gr. BaSO₄ = 18·16 per cent S.

(II.) 0·1093 " " 0·1447 " = 18·18 per cent S.

Required S = 18·30 per cent.

Enargite (As₄S₃Cu₃).

The oxidation was made in the same manner as in jamesonite :

0·1102 grm. mineral gave 0·2449 gr. BaSO₄ = 30·52 per cent S.

A second sample, oxidised with nitric acid, gave 31·00 per cent S.

Stephanite (Ag₅SbS₄).

This mineral was oxidised without difficulty. The conditions under which it was worked were similar to those of the preceding minerals :

(I.) 0·1044 grm. substance gave 16·69 per cent S.

(II.) 0·1109 " " 16·55 " "

Theory requires 16·20 per cent S.

Kobellite [(BiSb)₂S₅Pb₂].

The sulphur in this mineral was oxidised with ease :

(I.)	0·1136	grm. sub.	gave	0·1562	gr. BaSO ₄	=	18·38	p.c. S.
(II.)	0·1157	" "	" "	0·1594	" "	=	18·41	" "

The sample here oxidised was of the same material as that analysed by Dr. Keller (*Proc. Chem. Soc. Franklin Inst.*, 1, 127). On comparing the mean of his four sulphur determinations with the results obtained by the electrolytic method, it will be seen that the latter does not lack in completeness :

Current Oxidation.	Nitric Acid Oxidation.
Sulphur percentage.	18·37, 18·33, 18·46, 18·39
18·38—18·41	Mean, 18·39 per cent S.

Tetrahedrite (Sb,As)₂S₇(Cu₂Hg₂Fe,Zn)₄.

Quite a number of sulphur determinations and complete analyses of tetrahedrite of the above composition were made in this laboratory during the college year just closed. In all of these the chlorine method was employed for decomposition purposes. The percentage of sulphur found was 24·48 per cent. Samples of the same were then exposed to the action of a current of two ampères for

twenty minutes, and the sulphuric acid determined in the usual manner with these results:

- (I.) 0.1073 gr. mineral gave 23.81 per cent S.
(II.) 0.1096 " " 24.38 "
(III.) 0.1086 " " 24.23 "
(IV.) 0.1095 " " 24.37 "

Tetrahedrite seemed to require the full time (twenty minutes) for oxidation, for in several instances, where the current was interrupted after acting fifteen minutes, the alkaline solution became quite turbid upon acidulation.

Stannite ($\text{SnS}_4\text{Cu}_2\text{Fe}$).

The conditions here were the same as those already mentioned for the other sulpho-salts:

- (I.) 0.1087 grm. mineral gave 28.61 per cent S.
(II.) 0.1091 " " 28.02 "

Pyrrhotite ($\text{Fe}_{11}\text{S}_{12}$), Marcasite (FeS_2), and Pyrite (FeS_2).

The sulphur in the first of these three minerals is very readily changed to sulphuric acid. None of its iron passes into solution, so that the barium sulphate, after ignition, was perfectly white in colour. The residue, not soluble in water, showed no unoxidised sulphur:

- (I.) 0.1087 grm. mineral gave 0.3049 gr. BaSO_4 = 38.51 per cent S.
(II.) 0.1067 " " 0.3014 " = 38.79 per cent S.

By oxidation with nitric acid the sulphur found was 38.78 per cent S.

An exceedingly pure specimen of marcasite was exposed to the action of the current. Its sulphur was rapidly and completely oxidised:

0.1043 grm. substance gave 0.4056 gr. BaSO_4 = 53.40 per cent S. Required S = 53.33 per cent.

While these sulphides of iron parted with their sulphur with great ease, pyrite held half of its sulphur content quite tenaciously, notwithstanding it was exposed to the influence of much more powerful currents than the other two minerals.

(I.) 0.1667 grm. pyrite and 20 grms. KOH were exposed for ten minutes to the action of a current giving one ampere per minute. The crucible served as anode for half the time. The sulphur that was oxidised equalled 24.53 per cent.

ILLUSTRATIONS OF SEWAGE DECOMPOSITION IN STREAMS.*

By J. H. LONG.

DURING the last four years I have had occasion to carry out a lengthy investigation on the question of pollution of streams in Illinois, and in the progress of the work have observed certain points which I consider of interest to chemists dealing with analytical problems of similar nature.

This work was undertaken by authority of the State Board of Health, and since its beginning I have examined nearly 1000 samples. The results reached in a preliminary examination were presented to the Board in 1887. A few of them were explained in a paper in the *American Chemical Journal*, vol. x., No. 1, while the methods employed and tabulated results of the whole will appear in a future annual report of the Board.

The largest part of the work consisted in a study of the Illinois river from its sources to its mouth, and it is only with this part of the subject that I have to deal here.

At all seasons of the year the upper Illinois river receives a good part of its water from Lake Michigan through a canal flowing south-west from Chicago to

Joliet, when a union with a small stream known as the Des Plaines river is made. A few miles further toward the south-west these waters are joined by those from the Kankakee and Du Page, thus forming the Illinois proper. The watershed separating the basin of Lake Michigan from that of the Mississippi is very low, and is but a few miles from the lake. The canal referred to is fed by pumps, the water being drawn through the city and discharged by these pumps toward the west at the rate of 50,000 cubic feet per minute. The water in going through the city receives about three-fourths of its sewage, and in the canal flows undiluted to Joliet, a distance of 33 miles.

It will be seen, therefore, that we have here a most interesting problem. We have given a stream, highly contaminated at its source, and are able to follow and measure changes in the amount of contamination for many miles. In my first series of experiments, completed during the summer of 1886, very curious and important results were obtained. That season was unusually warm and dry, the rainfall in the part of the state under consideration being the lowest recorded in 15 years, and it was therefore possible to measure changes in the flowing river water, undisturbed by dilution of rain.

In the tests of that season, the determinations made were free and albumenoid ammonia and oxygen consumption by the Kubel method. The following mean results were obtained, expressed in parts per 1,000,000:

	Free Ammonia.	Albumenoid Ammonia.	Oxygen consumed.
Bridgeport	17.44	1.195	20.58
Lockport, 29 miles..	10.23	0.669	11.30
Joliet, 33 "	6.93	0.408	7.79
Ottawa, 81 "	0.382	0.237	5.57
Peoria, 159 "	0.035	0.187	4.85

Between Bridgeport and Joliet the dilution was practically zero during the whole season. Between Joliet and Ottawa the Illinois receives the water of the Kankakee, Du Page, and Fox, so that at the last named place it was estimated that the canal water was reduced to 43 per cent of the whole. But as a part of the diluting water came from a marshy region, it was by no means free from organic matter. Besides, some town drainage entered the stream between the two places. It is, therefore, probable that a reduction in organic matter took place between these points. The proportion of canal water, in the whole, was but slightly changed between Ottawa and Peoria, while some drainage entered at the town of LaSalle. We can trace, therefore, a very remarkable decrease in organic matter between the contaminated source at Bridgeport and the city of Peoria. From a study of all the facts bearing on the case, I have held that this change was due chiefly to oxidation (using this term in the broad sense to include changes brought about by micro organisms) rather than to sedimentation.

During the following winter these mean results were obtained, expressed in parts per 1,000,000:

	Free Ammonia.	Albumenoid Ammonia.	Oxygen consumed.
Bridgeport	9.7	3.7	22.4
Joliet	6.5	2.2	11.3
Ottawa	4.7	0.75	9.0
Peoria	1.7	0.43	6.45

In this table the increased amount of albumenoid ammonia with smaller amount of free ammonia at Bridgeport is apparent, and is, of course, due to the fact that decomposition is slower at a low temperature, and hence the sewage reached the pumps in a less advanced stage of oxidation. The large amount of albumenoid ammonia at Joliet is worthy of note at a time when sedimentation could accomplish the best results. The very slow decrease in free ammonia must also be noticed.

As intimated above, these tests may be considered as preliminary to a more complete investigation begun May

* From the *Journal of Analytical Chemistry*, Vol. iv., Part I.

1st, 1888, and concluded in March, 1889. In this investigation water was collected once a week at the following places between the source of supply at Chicago and the Mississippi river: Bridgeport, Lockport, Joliet, Morris, Ottawa, LaSalle, Henry, Peoria, Pekin, Copperas Creek, Havana, Pearl, Beardstown, and Grafton, the last being at the mouth of the Illinois river. Parallel tests were also made of the water supplied by the various tributaries of the Illinois to determine the nature of the dilution. In this investigation, in addition to free and albumenoid ammonia and oxygen consumption, total solids, suspended matter, nitrates, chlorides, and hardness were determined. In the following table only those data important for the present purpose are given and for places where water was regularly collected. During the early part of the season the rainfall throughout Illinois was heavy, in consequence of which the streams were full at times, adding much to the dilution of the main river.

The amount of this dilution can be roughly estimated from the chlorine determinations along the main stream and in the tributaries.

Mean Results of Analyses. May to October, 1888, inclusive.
(In Parts per Million.)

Places.	N in Nitrates and Nitrites.	Cl.	Free Ammonia.	Albumenoid Ammonia.	O consumed.
Bridgeport	0.000	46.811	12.253	2.558	23.113
Lockport	0.000	46.120	10.882	1.990	16.230
Joliet	0.000	43.658	8.932	1.681	14.301
Morris	0.380	32.149	4.107	0.707	10.920
LaSalle	1.037	19.717	0.636	0.526	8.558
Henry	0.683	17.660	0.467	0.481	8.657
Peoria	0.8915	12.358	0.210	0.522	9.769
Pekin	0.795	16.152	0.645	0.650	9.410
Havana	0.731	11.583	0.342	0.430	8.142
Beardstown	0.62	7.524	0.202	0.380	7.354
Grafton	0.582	9.205	0.095	0.483	7.300

Mean Results of Analyses. January to March, 1889, inclusive.

(In Parts per Million.)

Places.	N in Nitrates and Nitrites.	Cl.	Free Ammonia.	Albumenoid Ammonia.	O consumed.
Bridgeport	0.000	62.934	8.925	2.806	26.502
Lockport	0.000	56.083	8.149	2.489	22.820
Joliet	0.000	57.717	8.488	2.666	21.717
Morris	0.000	28.748	4.716	1.587	10.666
LaSalle	0.942	13.105	1.456	0.637	8.582
Henry	0.962	11.691	1.059	0.404	8.626
Peoria	0.510	12.860	1.637	0.549	9.611
Pekin	1.259	11.792	1.591	1.015	13.358
Havana	0.414	9.277	1.078	0.585	9.234
Beardstown	0.966	6.933	0.762	0.357	5.505
Grafton	0.087	7.523	0.875	0.722	9.818

In explanation of some of the peculiarities of the above tables, it must be stated that while the rainfall during 1888 was much heavier than during 1886, the mean temperature was in a marked degree lower. The winter of 1888-89 was, however, much milder than that of 1886-1887. In comparing the summer tests of 1886 with those of 1888, we notice that at Bridgeport in the first-named year the free ammonia was much higher and the albumenoid ammonia much lower than during the second season. It is also clear that the rate of change in these products between Bridgeport and Joliet is different for the two seasons. I think this can be largely looked upon as an effect of temperature, as dilution, contamination, and agitation of water were practically the same within these limits through the two seasons. During the hot summer of 1886 much greater decomposition must have taken place in the Chicago sewers themselves than during the cooler one of 1888, so that in the first case the diluted sewage reached the pumps in a more advanced stage of oxidation than in the latter.

One would expect to find, under these circumstances, less free ammonia and more albumenoid than in a season when the oxidation conditions had been more favourable.

To follow the change in the sewage after it leaves Chicago in its flow toward the Mississippi, we must consider the character of the diluting water from the tributaries. The mean results obtained by analysis of these waters are given (see next page), in parts per million, as before.

The flow from the DuPage is very small during the summer and its effect on the Illinois can be left out of consideration.

The Kankakee, draining a marshy country, has a steady flow throughout the summer, and forms about 20 per cent of the Illinois water at Morris. Its character is shown by low chlorine and nitrates and high albumenoid ammonia and oxygen consumption. Between Morris and LaSalle the Fox enters and dilutes the Illinois largely, as indicated by the decrease in chlorine. The dilution by the Big Vermillion is not large. The high nitrates here are worthy of interest. The city of Streator and several coal mines drain into the stream. Below Peoria the tributaries of importance are the Sangamon and Spoon. I have no data for the latter, but the results for the Sangamon are given above. Perhaps 30 per cent of the flow at Beardstown comes from these two streams.

Aided by these data, we can now consider the main river. Between Bridgeport and Lockport, a distance of 29 miles, there is during the summer an evident disappearance of organic matter, as shown by change in the free and albumenoid ammonia and oxygen consumption. But during the winter the change is in a marked degree less. This is especially apparent if we notice that the chlorine tests during the winter show some dilution between the two places. From Lockport to Joliet the distance is four miles, but on its way the water passes through four locks and over two dams to point of collection. It is thus thoroughly agitated and aerated. During the summer the tests show a decrease in organic matter, but the winter examinations indicate, apparently, an increase, as shown by albumenoid ammonia. A slight increase in free ammonia is also found. These observations are of practical importance. They show, first, that at Lockport the decomposing matter was not yet in condition to respond most perfectly to the albumenoid ammonia test, and also that the free ammonia gradually produced had accumulated rather than decreased by fermentation. Dilute solutions of white of egg undergoing putrefaction yields its largest amount of albumenoid ammonia at the start, as shown by experiments carried out in my laboratory by Mr. Powers. (See *Journal of Analytical Chemistry*, Oct., 1889.) But it is conceivable that solids in suspension, or other nitrogenous matters more stable than white of egg, would yield their largest amount of albumenoid only after preliminary disintegration.

Between Joliet and Morris the distance is 22 miles, and on the way there is a dilution of about 20 per cent by water in which the numbers for albumenoid ammonia and oxygen consumption are high. A part of the drainage of Joliet enters here besides. Giving these points due weight, it will be seen that there is a large reduction of organic matter in this part of the stream during the summer. This is not chiefly due to sedimentation. It has been shown by engineers in charge of surveys along the Illinois river, that owing to sufficiently high velocity of the water, sedimentation does not take place here. During the winter the relative dilution from the Kankakee was much greater, about half the water at Morris coming from the last-named stream. When the character of the diluting water is remembered, it is plain that the nitrogenous matter has suffered no change between the two places. In the 37 miles between Morris and LaSalle there is a great decrease in free ammonia with increase of nitrates, but when the dilution of the Fox river is considered, it is plain that the change in albumenoid ammonia is not important. During the winter season the Fox

	Nitrogen in Nitrates and Nitrites.	Chlorine.	Free Ammonia.	Albumenoid Ammonia.	Oxygen consumed.
DuPage river, enters above Morris	0.307	5.786	0.417	0.346	4.743
Kankakee river, enters above Morris.. ..	0.094	1.015	0.114	0.585	12.661
Fox river, at Ottawa, above LaSalle.. ..	0.027	4.974	0.278	0.463	7.066
Big Vermillion river, at LaSalle, ab. Henry ..	3.348	5.461	0.129	0.341	6.914
Sangamon river, above Beardstown	0.755	3.609	0.053	0.285	5.480

river dilution was relatively greater, which lessens somewhat the apparent decrease in albumenoid ammonia at this time. It is true, however, that changes take place in this part of the river which in the warmer season took place above.

In the 28 miles between LaSalle and Henry no important changes have taken place.

At Peoria the river widens into a lake, which receives a portion of the drainage of the city. The point where the samples were taken for analysis was evidently not beyond the influence of this contamination. During the winter this was increased by the drainage from sheds at the distilleries at which 25,000 head of cattle were fed. The effect of this is shown in the Peoria water, but most clearly in that from Pekin, ten miles below. Especially interesting is the great increase in nitrates observed at this point, and after the addition of fresh contamination.

Between Pekin and Beardstown there is a gradual improvement in the river, as shown by both summer and winter tests. Below Beardstown the Illinois was often diluted by back water from the Mississippi, which made the result of analysis irregular and obscure.

From the above it is apparent that while a gradual loss in organic matter occurs all the way between Bridgeport and Peoria, the rate of change was far less rapid in the summer of 1888 than in that of 1886. This difference, I believe, is chiefly due to differences in temperature and rainfall, which act directly and indirectly to modify the rapidity of bacterial oxidation.

In a wet summer the contents of the Chicago sewers, besides being cooled by rainfall, are rapidly washed out into the canal leading to the pumps. In a season of little rainfall much matter remains long enough in the sewers to become greatly modified by decomposition, and consequently disappears rapidly when thrown into the main channel. These opposite conditions were illustrated in the summer seasons in which tests were carried out, and they doubtless can be duplicated in all large cities in which the sewers are built with but slight incline. Sedimentation cannot play a more important part in the apparent purification of these waters in summer than in winter. In fact, after the navigation of the canal closes in the early winter, precipitation can take place which was impossible during the warmer months. Yet the winter tests show practically no decrease in the organic matter between Bridgeport and Morris. It would appear, therefore, that the self-purification of a very cold water is a slow process, even when aided by sedimentation.

On the other hand, the very remarkable results obtained between Bridgeport and Joliet in our first season's work show that with a sufficiently high temperature the disappearance of organic matter may be very rapid, unaided to any great extent by sedimentation.

It is known that temperature differences of a few degrees make very important differences in the rates of bacterial multiplication in many cases, and consequently in their efficiency as filth destroyers, and giving proper weight to this fact, I think many of the discrepancies observed between different examinations of the same polluted water, made at different times, may be explained.

The appearance and increase in nitrates and nitrites in the Illinois river affords us an instructive illustration. Frankland and others have shown that they are not formed in fresh sewage, and we see here that they appear only after a flow of many miles.

With the slower disappearance of albumenoid ammonia and less abundant formation of free ammonia in the cold season, we notice the later appearance of nitrates and

nitrites. Investigation may show that the appearance of these compounds marks an important stage in the purification of a polluted stream.

It is probable that they are produced only after practically all the readily fermentable bodies have been more or less changed, as in presence of such matter denitrification can take place with destruction of nitrites, and evolution of nitrogen even. The greatly increased nitrates below Peoria after pollution by fresh drainage from the cattle sheds, would seem to disprove this view. But such drainage is rich in hippuric acid, and this body, as well as its derivative, glycocholic, is readily broken up. Besides, because of the comparatively simple nature of the cattle feed (distillery slops and hay), the other matters present here must be less complex than what we have in ordinary city sewage, and therefore sooner converted into ammoniacal and other simple compounds.

Investigations, such as I have given an outline of above, are very difficult because of the practical impossibility of controlling all the conditions of experiments. Irregularities creep in where least expected, and in consequence the results of single observations have but little value when taken alone.

The results of investigations extended through a season have a different value, and I believe we can draw conclusions from these experiments on the Illinois which can be applied to the study of polluted river waters in general.

NOTICES OF BOOKS.

The River Irwell and its Tributaries. A Monograph on River Pollution. By G. E. DAVIS and A. R. DAVIS. Manchester and London: J. Heywood.

WE have here a contribution to the question of river-pollution worked out upon one of the filthiest streams or stream-systems in the world. Perhaps in no other locality is such a dense population, and such an amount of manufacturing chemistry collected along rivers of such insignificant dimensions. Hence, the concentration of the foul waters is unquestionable.

The immediate occasion for the appearance of this work is the prospect that at no distant date the total liquid—it might be hazardous to say *water*—now flowing in the channel of the Irwell must find its way into the Manchester Ship Canal. The authors hold out the prospect that the canal and its docks will become pestiferous in summer, and that the first reach of 2½ miles in length will become one "vast settling tank."

The authors consider that the suspended matters are the *crux* of the question, and that their removal, even if we disregard the soluble impurities, would be a great improvement.

The chlorine they regard—in our opinion rightly—as not in a manufacturing district a measure of sewage contamination. Nine-tenths of all the chlorine present in the bleaching agents used in the water-shed of the Irwell reappears in the stream at Throstle Nest Weir. Upon the determination of nitrates in polluted waters they lay no high emphasis.

The tables giving a view of the composition of the Irwell at different points and of its tributaries will be very useful for reference. We find here the statement that the water of the rivers Irk and Medlock in time of drought is more polluted than the normal sewage of Leeds or of Salford. We are glad to find that Messrs. Davis protest

against the current notion that river waters in time of flood are exceptionally pure, and may be safely let "slip by" down stream.

We regret, however, to find the opinion expressed that "the authorities should require a certain standard of purity to be attained before a liquid of any kind is allowed to flow into a water course." The authors approach here unpleasantly near to the "standards" of the Rivers' Pollution Commissioners, the objections to which have been fully explained in the *CHEMICAL NEWS*.

The methods used at the "Manchester Technical Laboratory"—which is throughout kept well in view—are given in full, and are in the main those of Mr. Wanklyn.

The Heating and Lighting of London by Pipe Lines. An Open Letter to Walter Wren, Esq., L.C.C., on the Abolition of London Fog. By T. HOWELL WILLIAMS, F.C.S., L.C.C.

THAT London fogs are a great and a growing evil is very generally admitted, though their harmful results are probably exaggerated. For their abolition a variety of means have been proposed, and if the public hesitate it is because, on the one hand, they are nearly powerless in the matter, and on the other because they justly fear that every scheme suggested must lead to an increase of the intolerable burden of local taxation. We have been truthfully told that if we would give up our "cheerful" fire-places and adopt the Dutch earthenware stove, our consumption of coal could—speaking within the limit—be reduced to one-fourth of its present amount. This would, of course, involve a corresponding decrease in the products of combustion and would besides bring the Coal Exchange to its knees. The author estimates the present cost of the transit of coal together with the profits of the middleman and the dealer amount to at least £6,000,000 annually.

Another proposal, due to our late friend Peter Spence, of the Manchester Alum Works, was to erect centrally a tower of Babel, into which all the products of combustion should be drawn through the sewers, the gases of which would at the same time be disinfected by the sulphur fumes. W. A. Gibbs, of Gillwell Park, would likewise draw the smoke downwards into the sewers, by means of gigantic tidal fans, discharging it near the mouth of the river. Here, also, there would be simultaneous ventilation and disinfection of the sewer-system.

Whether the engineering difficulties involved would prove fatal to either of these two projects we are not in a position to decide. We fear that they have both been condemned without a fair trial.

It is here mentioned that "Dr. Carpenter and others have proposed a tax in the nature of a hearth tax." If it were needful to make manifest the absurdity and the injustice of this proposal we might show that the number of hearths in a house gives no clue to the yearly consumption of fuel in such house, and that the tenant-occupier, though he may, perhaps, not use half the hearths in his dwelling cannot close them up at his pleasure.

Mr. Howell Williams proposes "that gas should be made at the coal fields, as close to the pit's mouth as convenient, that it should be conveyed from the gas-works situate in the country up to the metropolis in suitable mains, that it should be stored in gas-holders as at present, and that it should be solely utilised for heating and lighting the metropolis, together with providing all the motive power required for driving engines and machinery."

It will be seen that the author proposes to introduce two kinds of gas—one for illumination and another for heating. Hence, two pipe lines would be necessary. There is the question as to the locality for the giant gas-works which would have to be erected in the country. Other things being equal, they would have to be erected as near to London as possible. They would have to be

situate where the supply of coal would be in no danger of early exhaustion or of temporary interruption by "strikes."

It will be necessary that the gas, whether for heating or lighting, should be purified from sulphur quite as thoroughly as the gas now supplied in London. Otherwise, if sulphur be a cause—say the main cause—of the "London particular" we should still have the same quantity of the sulphur oxides in our atmosphere as at present.

We must call attention to the following passage, premising that the italics are the author's own:—"Gas pipes laid through arable land, *if it is found desirable to lay them underground*, are not harmful to the land itself, but rather do a certain amount of good, as they assist in draining the country. If the joints are made perfect and well covered round with clay, they will effectually prevent any possible escape of gas." Suppose the sole supply of light and warmth to London dependent upon the integrity of a couple of pipes-lines extending for 100 miles: would not an army be required to guard them against intentional mischief? If placed underground the operation would have to be conducted with much greater care than in laying down our street mains, in which leakage is never absolutely excluded. The only safe method would be to bury them very deeply along the sides of roads.

As to the matter of expense, the question is not so much how the capital is to be obtained as how the interest on such a large sum is to be paid. Sanitary reformers—like reformers in general—are apt to forget that, however desirable some project may seem, communities, as well as individuals, may have to forego it if they cannot afford the outlay. Would not the existing gas companies consider themselves entitled to compensation if this scheme were carried out?

Inorganic Chemistry: Theoretical and Practical. A Manual for Students in Advanced Classes. By WILLIAM JAGO, F.C.S., F.I.C. London: Longmans, Green, and Co.

CONCERNING this work we must say substantially what we have remarked concerning not a few of its predecessors; chemical phenomena and laws are here, in the main, accurately described and laid down, but not more accurately than they may be found in other manuals. Hence we are compelled to ask, as we have asked in the case of not a few earlier manuals, *cui bono*?

A few oversights have slipped in. Thus we read that "the impure commercial hydrochloric acid is largely used for the formation of chloride of tin, SnCl_2 , a salt employed by the dyer and calico-printer." But impure acid invariably contains iron, which even in infinitesimal traces spoils certain colours, such as alizarin reds and pinks. Hence the makers of such preparations of tin are very careful to use the purest hydrochloric acid attainable.

On p. 361 the author, after mentioning the use of aluminium hydrate (better, soluble aluminium salts) for precipitating the impurities of sewage, goes on to say: "As a converse of this certain pigments called lakes are prepared by precipitating aluminium hydrate in the coloured solutions, when the colouring matter is carried down by the precipitates." Now these two applications of alumina are not one the converse of the other, but identical. The hydroxide, or more probably the basic salt, forms in either case an unstable combination in sewage with the impurities and in dye liquors with the tinctorial principles.

We feel a difficulty in harmonising the two following consecutive sentences:—"Glass, if well-made, is practically insoluble in water and acids, except hydrofluoric acid. Nevertheless, water dissolves glass in appreciable quantities."

The account of the production of ferrous sulphate in § 441 is not in accordance with general practice. The author writes:—"On heating alum schists containing

pyrites sulphates of alumina and iron are formed. On lixiviation and crystallisation ferrous sulphate separates as greenish crystals." The material used for the manufacture of ferrous sulphate is the soft pyrites of the coal formations, which are not heated but oxidised by prolonged exposure to air and rain.

The account of spectroscopic research here given is more complete than that contained in many elementary works, but we do not find any notice of the absorption spectra of solutions.

The only serious defect in this work, in our humble opinion, is the author's evident faith in the Science and Art Department, and, as a corollary, in the examination *regimé*. For the teachers and students of a nation to "model their work on lines of general treatment adopted by any "Department" seems to us a great misfortune, tending to stereotype, or we might say to ossify, the national intellect. The constitution of the Department does not escape foreign criticism. The Continent says that Britain places her army and navy under the rule of civilians, and in return places higher education in the hands of half-pay officers.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—As you have opened your columns to a discussion on a circular respecting the Fellowship of the Chemical Society, signed and issued on behalf of our committee by Mr. Lloyd and myself, I am requested to write and ask you to be so good as to publish the circular *in extenso*.

The letter of Mr. A. Philip is of the nature of an *ex parte* statement, and the committee feel that in fairness the circular should also appear in your valuable paper.—I am, &c.,

FRANK L. TEED.

"THE CHEMICAL SOCIETY.

"Those who have watched the elections to the Chemical Society during the past few years, cannot fail to have observed that persons are obtaining admission as Fellows who are in no way interested in the promotion of Chemistry, or who take advantage of the Fellowship for trade purposes, or whose admission is for other obvious reasons injurious to the Society and the Chemical profession.

"The Chemical Society having been in existence for fifty years, its Fellowship is known and appreciated as a qualification, while that of the Institute of Chemistry is as yet inadequately recognised. Hence, since the formation of the Institute of Chemistry, and largely owing to the greater difficulty in obtaining its Fellowship, the number of undesirable candidates for the Fellowship of the Chemical Society has increased.

"Injudicious admissions to the Chemical Society counteract to a great extent the beneficial effects of any steps taken by the Institute of Chemistry to raise the *status* of professional chemists. The attention of Fellows is therefore drawn to the necessity of maintaining the dignity of the Fellowship of the Chemical Society, and of preventing its prostitution to trade purposes, whilst retaining its legitimate professional use.

"It has been stated that the simplest method is to blackball unsuitable candidates. This practice has not recently been properly and judiciously utilised by the Fellows of the Society. It can, moreover, only be carried out by those Chemists who are resident in London, and while throwing upon them an unpleasant duty, which should be unnecessary, it does not provide adequate means for the exclusion of undesirable persons.

"Careful attention to the two following courses of action, and unanimity in carrying them out, are in the first instance urged upon the Fellows:

"(1)—The exercise of greater care in recommending candidates, and the refusal to sign any certificate unless the candidate and his object in wishing to join the Society are well known to the Fellows applied to.

"(2)—That Fellows should vote against those whose scientific claims are obviously insufficient to entitle them to the Fellowship, or who from any other cause known to them, ought not to be elected.

"While these steps are open to the Fellows, the Council should be requested to consider the matter fully, and to frame such by-laws as may be required to place the method of admission upon a sound and satisfactory basis.

"It should be noted that under the present system of election, no opportunity is afforded for making known to the Fellows any information which might assist their judgment while balloting.

"The following recommendations are suggested to the Fellows for consideration, with the view of calling the especial attention of the Officers and Council to them, as worthy of incorporation in the by-laws:

"(a) Exact definitions of the qualifications requisite in candidates for the Fellowship.

"(b) The Council to consider every application for admission to the Fellowship: to be empowered to inquire into the suitability of candidates, and to invite and receive strictly confidential communications from Fellows who may know anything against any proposed candidate.

"(c) The Council to submit to the Fellows, at stated times, a list of those candidates whom they consider suitable for election, and also a list of those with regard to whom they make no recommendation. Full particulars as to the candidates to be supplied with each list.

"The final election of candidates must remain in the hands of the General Body of Fellows, and be carried out by a properly organised system of balloting after three 'Readings' before the Society.

"Steps are being taken to ensure the carrying out of the recommendations made herein during the ensuing Session.

"Fellows are requested to sign the annexed form, striking out any recommendations with which they do not agree, and adding any remarks that they may consider desirable; and to return it to either of the Honorary Secretaries to the Committee,

"FREDERICK J. LLOYD, 4, Lombard Court, E.C.

"FRANK L. TEED, 15, Victoria Street, S.W.

"October 1st, 1890.

"I have received your communication, dated 1st Oct., 1890, relating to the present method of electing Fellows of the Chemical Society. My views on the subject are understated. I am of opinion:—

"1. That the taking of immediate steps to maintain the dignity of the Fellowship of the Chemical Society is necessary.

"2. That Fellows should refuse to sign any Certificate unless the Candidate, and his object in wishing to join the Society, are well known to them.

"3. That Fellows should not recommend, and should vote against, those whose scientific claims are obviously insufficient to entitle them to Fellowship, or who, from any other cause known to them, ought not to be elected.

"4. That the Council should be requested to consider the matter, and to frame such by-laws as may be required to place the method of admission upon a sound and satisfactory basis.

"5. That such by-laws should contain exact definitions of the qualifications requisite in candidates for the Fellowship.

"6. That such by-laws should provide that the Council shall consider every application for admission to the Fellowship, and shall be empowered to inquire into the

suitability of Candidates, and to invite and receive confidential communications from Fellows who may know anything against any proposed Candidate.

"7. That the Council should submit to the Fellows, at stated times, a list of those Candidates whom they consider suitable for election, and also a list of those with regard to whom they make no recommendation, and that full particulars as to the Candidates should be supplied with each list.

"8. That the final Election of Candidates should remain in the hands of the General Body of Fellows, to be carried out by a properly organised system of balloting after three 'readings' before the Society."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 13, September 29, 1890.

Absorption of Carbon Monoxide by Earth.—M. Berthelot.—The author refers to the well-known fact that it is dangerous to enter the galleries of a mine immediately after an explosion, or to even go into the cavities hollowed out by the explosion of large bombs, especially if gun-cotton or melinite has been used. Carbon monoxide is the cause of most of these accidents which have been observed in gaseous mixtures so rich in oxygen that a candle will burn in them readily. This result has been attributed to some specific property in consequence of which the soil retains carbon monoxide more persistently than other gases. The carbon monoxide thus occluded is gradually given off, and there is no reagent capable of absorbing it under these conditions. The only remedy is a sufficient and prolonged ventilation.

On the Acetylene Condensed by the Effluve.—M. Berthelot.—The condensation of acetylene effected by the effluve is quite different in character from that which takes place under the influence of heat (at about 400° to 500°). The pyrogenous polymerisation of acetylene produces especially benzene, but it takes place with a considerable loss of energy (+171 cal.), which explains the great stability of the product. On the contrary, the product condenses in the cold under the influence of the effluve, retaining a much stronger proportion of energy, as is shown by the explosive (exothermic) character of their decomposition.

Electric Spectrum of Gadolinium Chloride.—Lecoq de Boisbaudran.—The author, on causing the spark of his induction-coil with a long wire to strike over the hydrochloric solution of gadolinium, obtains a beautiful spectrum, consisting chiefly of bands having numerous rays, many of which are strongly degraded towards the red. With Demarcay's short-wire coil and a very small interpolar space the bands disappear, and there is developed a new spectrum composed of definite rays, numerous and very brilliant. With the same short-wire bobbin, but with the poles placed at the greatest possible distance from each other, the band-spectrum is developed with extraordinary splendour. The spectral reaction of Gd is therefore very decisive. The author gives a long description of the spectrum furnished by the spark of the long-wire coil. Besides these bands, there are also seen traces of some of the principal narrow rays of the high-temperature spectrum which is developed when the short-wire coil is used without elongating the spark.

On the Equivalent of the Terbias.—Lecoq de Boisbaudran.—In a former investigation (*Comptes Rendus*,

Feb., 1886, p. 395) the author determined the equivalent of his best earth, Z β (a very deep brown terbia) by weighing the sulphate obtained from a given weight of the earth. The minimum value obtained was eq.=124.7; atomic weight of the metal =163.1: but the corrections of the weights subsequently mentioned (C. R., September, 1888, p. 492; and September, 1890, p. 410) were not employed, and the earth was simply weighed, after ignition to full redness, which leaves the proportion of the oxygen of superoxidation somewhat uncertain. The author has repeated this determination, weighing the sulphate obtained from a known weight of Z β O₃, but after igniting it to whiteness and studying the absorptions excited by the substance after the extinction of the fire. The oxygen of superoxidation (much less than after mere ignition to redness) was determined, and its weight deducted from that of the earth. He thus obtains lower values.

	Equiv.	Atomic weight.
First experiment	122.63	159.95
Second "	122.01	159.01
Mean	122.32	159.48

Further determinations could not be effected from the want of sufficient material. The earth Z β , ignited to whiteness in a covered crucible, but over the oxidising flame of a gas blowpipe, dissolves slowly in dilute hydrochloric acid with the aid of heat. It still retains $\frac{0.16}{100}$ of oxygen of superoxidation; its colour is much lighter, but still very yellow.

A New Safety Lamp for Mines.—Charles Pollak.—A rectangular box of ebonite contains accumulators of the Pollak system; it rests upon a metal plate. An ebonite lid serves as support for a glow-lamp enclosed in a cylinder of thick glass. The whole is covered with a metal top, fixed closely by means of pins. A leaf of soft caoutchouc, introduced between the top and the box renders the junction hermetic. Into the lid are inserted rods of an inoxidisable metal, which pass through it and support at their bases contacts of platinum, which meet the platinum contacts of the accumulators, and which have at their summits springs, one of which is in metallic connection with a foot of the lamp. The other foot of the lamp is insulated, and can be brought in contact with a pole of the accumulator by means of a needle introduced into a horizontal channel made in the lid. As the contacts are in the interior of the box and the lid, neither the opening nor the closing of the current can cause an explosion; hence the lamp can be either ignited or extinguished in an inflammable atmosphere. If the system is dismounted, or if the glass globe of the glow-lamp is broken, the lamp is extinguished. The model exhibited weighed 1800 grms., and gives a perfectly constant light of 0.7 to 0.8 candle-power for twelve hours.

The Properties of the Natural Colouring Principles of Yellow Silk, and on their Analogy with Vegetable Carotene.—Raphael Dubois.—According to the researches of Roard and Mulder, the colour of yellow silk is due to a resinoid matter containing a red pigment, insoluble in water, though soluble in alcohol, ether, and the volatile and fatty oils. In fact, yellow silk contains several colouring-matters, some of which the author has extracted. 1. A golden-yellow pigment, soluble in solutions of potassium carbonate, and precipitated by acetic acid in excess. 2. Crystals of a reddish yellow by transmitted, and of a brownish red by reflected light. 3. An amorphous lemon-yellow matter. 4. Lemon-yellow octahedral crystals, like those of sulphur. 5. A deep greenish blue pigment present in very small quantity. The mixture of the colouring-principles 2, 3, and 4, which the author has not yet been able to separate, on account of the small quantity of material at his disposal, agrees in its characters with carotene.

MISCELLANEOUS.

Robbery of Platinum at Messrs. Dunn and Co., Stirling Chemical Works, West Ham.—The following circular has been sent out by Messrs. Dunn and Co.:—"Six Platinum Dishes were stolen from our premises on Sunday, October 12th. 3 Dishes, 10½ inches diameter by 8½ inches deep, weighing about 80 ounces each; 3 Dishes, 8½ inches diameter by 6½ inches deep, weighing about 50 ounces each. If you should hear of any attempt to dispose of such platinum (in scrap or otherwise), we would thank you to acquaint the Police and advise us by telegraph. By so doing you would confer a great favour."

Literary Announcements.—A very important new work, entitled *The Mechanical Engineers' Office Book for Machine and Boiler Construction*, will shortly be issued by Messrs. Crosby Lockwood and Son, London. The work is written by Mr. Nelson Foley, and illustrated by fifty specially prepared plates, in large folio.—The same publishers also announce *The Colliery Managers' Handbook: a Guide to Practical Coal Mining*. By Caleb Pamey, M.E., with about 400 Plans and Diagrams. Medium 8vo.—*The Analysis and Valuation of Fuel*, Solid, Liquid, and Gaseous; a Manual for Chemists and Engineers. By H. J. Phillips, F.C.S. Crown 8vo.—*Asbestos: Its Properties, Occurrence, and Uses*. By R. H. Jones. Illustrated with Collotype Plates. Crown 8vo.—*Ventilation: a Practical Handbook for Sanitary Engineers, Architects, &c.* By W. P. Buchan. Fully Illustrated. Crown 8vo.—*The Number, Weight, and Fractional Calculator*, being the third edition of "The New Calculator." By William Chadwick. Thick 8vo.—*Electric Light: Its Production and Use*. By J. W. Urquhart. Fourth Edition. Revised and extended. Crown 8vo.—*A Handbook for Young Brewers*. By Herbert Edwards Wright, B.A. Entirely New Edition. Re-written and enlarged.—Also the following New Edition in Weale's Rudimentary Scientific Series: *Portland Cement for Users*. By Henry Faija, M.Inst.C.E. Third Edition. Corrected and enlarged.

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The Contractor will be required to enter into an Agreement for the due fulfilment of his contract.

Printed Forms of Tender may be had on application to the Master, and no Tender in any other form will be received.

The Price to be stated in words at length, and Tenders to be delivered at the Board Room on Tuesday, the 28th day of October inst., at, or before, six o'clock in the evening, after which hour Tenders cannot be received.

The Guardians reserve the power of rejecting any Tender or article on delivery.

By order of the Board,

A. C. COOLE, Clerk.

9, Carfax, Horsham,
October 6th, 1890.

Chemists, Druggists, Perfumers, Store Proprietors, and others.—By order of the Trustees, under Deed of Assignment.—Estate of G. F. Fuller, Sun Street, Hitchin.

JOSEPH DAWE is instructed to offer for SALE by Tender the whole of the extensive stock herein of PATENT MEDICINES, Drugs, Perfumery, Chemist's Sundries, and Toilet Requisites, amounting at cost or stock-book prices to about £350. The Tenders will be opened on Thursday next, Oct. 30, 1890, at twelve o'clock, at the offices of Messrs Oscar Berry and Carr, Chartered Accountants, Monument House, Monument Yard, E.C. The goods can be inspected on the premises, and full details ascertained on application to Oscar Berry, Esq., C.A., Monument House, E.C.; Geo. White, Esq., C.A., 14, Old Jewry Chambers, E.C.; and to Joseph Dawe, Auctioneer, 7, Eastcheap, E.C.

Wanted, a Situation as Assistant Analyst in an Analytical or Manufacturing Laboratory. Has been three years studying General and Organic Analysis, and Assaying, and has some knowledge of Gas Analysis and Practical Physics. Certificates for Chemistry from the Science and Art Department, London; good references.—Address, G. H. B., 48, Broadmead, Bristol.

THE CHEMICAL NEWS.

VOL. LXII. No. 1614.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

In dealing with a mixture of two oils, the following equation will be found very useful. The mixture contains linseed oil and lard oil. The iodine absorption per cent of linseed oil is 170, and for lard oil is 52.5 per cent; x and y are the quantities respectively of each oil required to give an iodine absorption = 84.5 per cent—

$$\begin{aligned}(170 \times x) + (52.5 \times y) &= 84.5(x + y), \\ 170x - 84.5x &= 82.5y - 52.5y, \\ 85.5x &= 32y,\end{aligned}$$

i.e., 117.5 parts of the mixture contains $85.5 \times x$ and $32 \times y$ of the separate oils. We simplify by making $y = 1$. The problem now is:—How much lard oil, = 52.5 per cent, must be mixed with 1 part linseed oil, = 170 per cent, to yield a mixture = 84.5 per cent iodine absorption.

$$\frac{170 + 52.5x}{x + 1} = 84.5,$$

$$\begin{aligned}170 + 52.5x &= 84.5x + 84.5, \\ 32x &= 85.5 \therefore x = 2.67;\end{aligned}$$

hence, 1 part linseed oil and 2.67 lard oil is the mixture required for—

$$\begin{aligned}52.5 \times 2.67 &= 140.17 \text{ lard oil} \\ 170 \times 1.0 &= 170.0 \text{ linseed oil}\end{aligned}$$

$$3.67 \quad 310.17$$

adding $\frac{310.17}{3.67} = 84.5$, the iodine absorption required; then—

$$\frac{3.67 : 2.67 :: 100 : 72.8 \text{ per cent lard oil}}$$

and—

$$72.8 \times \frac{52.5}{100} = 38.22, \text{ iodine absorption for lard oil}$$

$$27.3 \times \frac{170}{100} = 46.41, \quad \text{,,} \quad \text{,,} \quad \text{linseed oil}$$

$$84.63 \quad \text{,,} \quad \text{,,} \quad \text{mixture.}$$

Supplementing the calculations given in the CHEMICAL NEWS, vol. lxii., p. 125, the following simple treatment gives direct results:—The numbers for the iodine absorption of each oil, if subtracted from the averages of the iodine absorption of a mixture, and 100, will give the percentage quantity of each oil.

Mean of 100 and 96.4 = 98.2.

$$\begin{aligned}98.2 - 42.8 &= 55.42 \text{ per cent sesame oil} \\ 98.2 - 53.6 &= 44.6 \quad \text{,,} \quad \text{olive ,,}\end{aligned}$$

Mean of 100 and 84.5 = 92.25.

$$\begin{aligned}92.25 - 19.95 &= 72.3 \text{ per cent lard oil} \\ 92.25 - 64.6 &= 27.65 \quad \text{,,} \quad \text{linseed oil.}\end{aligned}$$

The figures obtained in this way are confirmed by other methods. In dealing with a mixture of more than two oils, we must introduce other functional equations for exact results.

Let $M = 100$ be a mixture of olive, lard, and linseed oils, with iodine absorptions 84.5 per cent, 52.5 per cent, and 170 per cent respectively, and let 84.5 per cent be the iodine absorption of M .

Let 58.5° C. be the rise of temperature (Maumené's reaction) observed on M , and let 42°, 42°, and 133° C. be the rise of temperature noted on each oil respectively.

Now, as olive oil and lard oil each give a rise of 42°, and linseed oil 133°, a rise of temperature above 42° is due to linseed oil; knowing, then, the weight of linseed oil, we can eliminate from the iodine absorption of M the absorption due to linseed oil. The remaining iodine absorption is due to a mixture of olive and lard oils, and from which we can calculate the quantities of each.

Let x , y and z be the unknown quantities of each oil respectively, then—

$$x + y + z = M = 100 \quad \dots \dots \dots (1).$$

$$100 \times 84.5 = 84.5x + 52.5y + 170z \quad \dots \dots \dots (2).$$

and—

$$100 \times 58.5^\circ = 42^\circ x + 42^\circ y + 133^\circ z \quad \dots \dots \dots (3).$$

Combining equations (1) and (3)—

$$42(x + y) + 133z = 58.5 \{ (x + y) + z \}$$

$$x + y = 4.51z.$$

Substitute this for $x + y$ in equation (1)—

$$4.51z + z = 100.$$

$$\therefore z = 18.1 \text{ per cent linseed oil;}$$

whence—

$$x + y = 100 - 18.1 = 81.9 \text{ p.c. olive and lard oils.} \quad (4).$$

From equation (2)—

$$84.5x + 52.5y + (170 \times 18.1) = 8450,$$

subtracting 170×18.1 from each side of this equation, we get—

$$84.5x + 52.5y = 5373 \quad \dots \dots \dots (5).$$

From equation (4), $y = 81.9 - x$, substitute, in equation (5), this value of y :—

We have $32x = 1057.2 \therefore x = 33.0$ per cent olive oil, and $81.9 - 33.0 = 48.9$ per cent lard oil.

Collecting results :—

			Actual mixture.*
Olive oil ..	33.0	I. abs. = 27.88	Olive oil .. 33.3
Lard ,, ..	48.9	,, = 25.67	Lard ,, .. 48.5
Linseed oil ..	18.1	,, = 30.77	Linseed oil .. 18.1
	100.0		84.32
			100.0

My attention was directed to a mixture of these oils, some time ago, by a friend, who said it was used in soap-making, and was purchased as olive oil of a special grade. As such a mixture has an industrial application, this method of equating its composition may be useful.

A mixture of these oils may be complicated by adulterations of olive or lard oils, or perhaps both, by cotton-seed oil. In every case, we must first be sure that we have obtained most reliable evidence of the individual oils contained in a mixture.

THE ALCOHOL TEST FOR PURE CASTOR OIL.

By J. ARTHUR WILSON.

CASTOR oil differs in many respects from most fixed oils especially in consisting largely of the glyceride of ricinoleic acid, which is soluble in absolute alcohol. Hence this reagent can be used for the detection of impurities in castor oil. Like most other tests of a similar kind, it is not of much use for the detection of small quantities of foreign oil, owing to the solvent action of the dissolved castor oil on the small proportion of foreign oil that may be present.

The British Pharmacopoeia directs that pure castor oil shall be soluble in an equal measure of absolute alcohol and twice the measure of rectified spirit.

* Made by taking 1 part olive oil and 2 parts of the mixture of lard oil and linseed oil referred to (CHEMICAL NEWS, vol. lxii., p. 179).

According to Mr. Allen ("Commercial Organic Analysis, vol. ii., 128) this is correct at 30° C., providing spirit of exactly 0.838 gravity be used. I have examined a number of samples of both commercial and medicinal castor oil, strictly at 30° C., and by a spirit of exactly 0.838 specific gravity, and find that at exactly 30° C. the oil is not completely soluble, but that the temperature of solution varies between 38° and 43° C. I may say that the oils I used satisfied all other requirements as to purity.

In carrying out the alcohol test, it is best to operate as follows:—One measure of the castor oil under examination is mixed thoroughly with two volumes of spirit of exactly 0.838 specific gravity, and then heated, stirring well with a thermometer till complete solution. In the case of genuine castor oil this will be between 38° and 43° C., possibly lower than the former; whilst if any foreign oil be present, the temperature will be much higher; and in gross adulteration, some oil may not be dissolved even at the boiling-point of the mixture.

Tottington, Oct. 20, 1890.

THE SEPARATION OF TIN AND ANTIMONY.*

By H. N. WARREN, Research Analyst.

A CONVENIENT quantity of the sample, either an ore or slag, as the case may admit of, having been reduced to powder by the usual method, is introduced into a nickel crucible of convenient dimensions, and intimately mixed with about ten times its weight of a mixture of sodium carbonate and one of borax, the decomposition being brought about by the application for a few minutes of a full red heat from an ordinary foot blowpipe. When all necessary reaction has terminated, the contents may be advantageously poured on to the surface of an iron slab or other incombustible substance. The melt thus obtained is rapidly and completely dissolved by the aid of a small quantity of dilute HCl, introduced into a flask of known capacity, together with the small quantity which still adheres to the sides of the crucible, which is rapidly detached by pouring into the same a further quantity of dilute acid and gently warming. The contents of the flask are now diluted to the containing mark, and a known quantity withdrawn by the aid of a pipette, which is received into an accompanying flask and saturated with a stream of SH_2 gas. Tin, antimony, and similar metals of the same group, becoming consequently precipitated as sulphides. The mixed precipitates thus obtained are filtered and collected by means of a plug of cotton inserted in the neck of a glass funnel; the cotton, with its contents, after being once washed, is dislodged and received into a vessel containing a strong solution of NaHO, the same being raised and maintained for a few minutes at the boiling-point; the tin and antimony sulphide passing into solution as sulphostannate and sulphoantimoniate of soda. The soluble tin and antimony compounds thus obtained are separated by re-filtering, as in the previous case, and divided into two separate portions, being received, for convenience sake into two flasks, and labelled A and B portions. To the A portion is introduced a somewhat large excess of oxalic acid, and the solution allowed to boil until the small quantity of antimony sulphide that remains presents a pure orange-red colour, characteristic of that compound; the precipitate being collected in the usual manner, and decomposed in a porcelain crucible at a very low red heat, weighing as Sb_2O_3 and calculating to percentage of antimony. To the second, or B portion, is added an excess of dilute HCl, and the whole gently warmed; the re-precipitated sulphide thus obtained treated precisely the same as in the previous instance, weighing as oxides. The total amount of tin being obtained by

deducting the former weight of precipitated oxide obtained from the A portion, from that of the mixed oxides obtained from the second, or B, portion, and calculating by its respective formulæ.

The speed and accuracy obtained by the method foregoing largely depends upon the judicious use of the borax employed towards the commencement of the operation, whereby not only a most readily fusible compound is obtained, but, at the same time, being readily soluble in acid; inasmuch that the author has not unfrequently effected a complete assay of from twenty to thirty samples in a day; whereas, by any of the ordinary methods hitherto employed, one-tenth of that quantity would be attended by considerable labour accompanied by more or less inaccuracy.

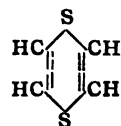
Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

BIOPHENE.*

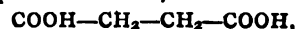
By LOUIS E. LEVI, Ph.D.

THE gap which now separates the fat from the aromatic series is being rapidly filled. The great researches upon pyridine, pyrrol, furfuran, thiophene, and other groups of bodies similarly derived from the fat series, have already shown to chemists that the words "fat" and "aromatic" must soon be changed to some more appropriate terms. All the reactions which the above groups possess, although they are derived from bodies in the fat series, show them to be closely related to the aromatic compounds.

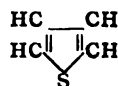
The actions of acids, halogens, and all other reagents, upon these groups, are more marked, and progress more easily and rapidly, than upon the aromatic compounds. The thiophene discovered by Victor Meyer being the first body containing sulphur and possessing the properties of aromatic bodies, is of especial interest. During the time the writer had the pleasure of working under Victor Meyer, and later of working with him, the idea of a body similar to benzol, in which two "CH" groups are replaced by two sulphur atoms, was first suggested. The interest in the question, whether a body with the symbol—



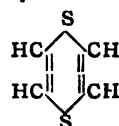
would also possess the properties of an aromatic compound, was very great. Since the action of phosphorus trisulphide upon succinic acid,—



forms thiophene,—



so thiodiglycollic acid, $\text{COOH}-\text{CH}_2-\text{S}-\text{CH}_2-\text{COOH}$, should, under the same conditions, produce the body which we will call "biophene":—



The probability of the formation of biophene by this reaction is increased by the fact, that while succinic acid and phosphorus trisulphide yield thiophene, thiodiglycollic acid is composed of two half molecules of succinic acid

* The Chemical Trade Journal Prize Essay.

* From Technology Quarterly, vol. iii., No. 2.

joined together by an atom of sulphur. Biophene, is produced, as was expected, by the above reaction, but only under certain conditions.

The method of distilling the acid with the phosphorus trisulphide, the way in which thiophene is made, yields an impure product containing very little biophene, but yet sufficient to show the characteristic indophenin reaction. In order to obtain biophene in sufficient quantity and purity, the method of its preparation was modified.

Preparation of Biophene.

Five grms. of thiodiglycolic acid are mixed with ten grms. of phosphorus trisulphide, and placed in a tube, closed at one end, with 15 to 20 c.c. of ether. The tube is then closed with a fine capillary, placed in an oven, heated two hours at a temperature of 170° C. After cooling, the capillary is opened to allow the escape of the hydrogen sulphide formed. The contents of the tube, which has an odour not unlike the secretions of a skunk, is placed in a separating funnel, and washed with potassium hydrate. The alkali is then drawn off, and the remaining oil dissolved in ether and dried with chloride of calcium. After drying thoroughly, the ether is evaporated and the substance fractionated. The oil passes over in fractions between 140° and 170° C., accompanied by a slight decomposition. By re-fractionating, an oil having the constant boiling-point 165—170° is obtained. This product, when mixed with sulphuric acid, and a crystal of isatin added, gives a beautiful violet colour, the characteristic indophenin reaction of the thiophenes. The analysis showed that this oil was biophene.

0.180 gr. of the oil oxidised with HNO₃, yielded 0.7208 gr. BaSO₄.

	Found.	Theory for C ₆ H ₈ S.
Sulphur	55.00	55.17

Aceto-bienone, C₆H₄S₂COCH₃.

To a mixture of 1 grm. of biophene, 10 grms. of petroleum ether, and 1 grm. of acetyl chloride, aluminium chloride is slowly added. A reaction begins immediately, accompanied by the evolution of hydrochloric acid gas. If the flask is shaken every five minutes, the reaction will be quickly finished, and the aluminium compound of the ketone will settle to the bottom of the flask. When, on further addition of aluminium chloride, no more hydrochloric acid gas is given off, the product is warmed about fifteen minutes upon the water-bath, and the petroleum ether poured off. The thick oily mass is then decomposed with ice and water, and purified by distilling with steam. The distillate is extracted with ether, and dried over chloride of calcium. On evaporating the ether, there remains a heavy slightly coloured oil, whose odour is very aromatic and like that of aceto-thienone.

Aceto-bienone distils at a temperature above 300° C., at the same time decomposing. The action of light upon it turns it dark brown. In order to characterise aceto-bienone as a ketone, the phenylhydrazine compound was made.

Aceto-bienone and Phenylhydrazine.

Molecular weights of aceto-bienone, phenylhydrazine, and anhydrous sodium acetate are heated upon the water-bath, with a little water, about six hours. On cooling, beautiful red - coloured needles precipitate, which upon re-crystallising out of alcohol are obtained pure. The phenylhydrazide has a melting-point of 128°, and is soluble in alcohol and ether.

0.156 gr. of the salt, oxidised with HNO₃, yielded 0.2905 BaSO₄.

	Found.	Theory for C ₆ H ₄ S ₂ C $\begin{smallmatrix} \text{CH}_3 \\ \text{N}_2\text{HC}_6\text{H}_5 \end{smallmatrix}$
Sulphur	25.6	25.8

Oxidation of Aceto-bienone.

To 1 grm. of aceto-bienone take 2.55 gr. KMnO₄, and add 15 c.c. of a 14 per cent KOH solution for every 50

c.c. of a 2 per cent KMnO₄ solution. This mixture is placed in a flask with a return cooler attached, and agitated continually. The reaction begins immediately, and the liquid assumes a dark green colour. As soon as the green colour disappears, the substance is heated on the water-bath for thirty minutes, when the oxide of manganese which is formed will settle to the bottom, leaving a clear liquid. The oxide of manganese is removed by filtration, and the liquid acidified with sulphuric acid and extracted with ether. After the ether solution is evaporated, an oil remains, which, on standing, crystallises. The crystals are purified by crystallisation from alcohol or water. The water solution shows the characteristic acid tests with litmus-paper and sodium carbonate. The yield being small, an analysis could not be made.

Phenylbienylketone, C₆H₅>CO, C₄H₃S₃

is formed by the action of benzoyl chloride upon biophene in the presence of aluminium chloride, in the same way as the above-described aceto-bienone. Phenylbienylketone is a dark brown oil, having a boiling-point of 241° C., and is soluble in alcohol and ether.

0.2933 gr. oil yielded 0.6310 gr. BaSO₄.

	Found.	Theory for C ₆ H ₅ >CO, C ₄ H ₃ S ₃
Sulphur	29.18	29.09

Nitrophenylbienylketone.

Two grms. of phenylbienylketone are slowly mixed, drop by drop, with nitric acid (sp. gr. 1.62), cooled by a freezing mixture of Glauber's salt and hydrochloric acid. As soon as the two substances come in contact, a violent reaction takes place, and the oil is completely dissolved. On cooling, the product of the reaction is diluted with water, and a light yellow mass precipitates. The precipitate is then placed upon a filter, and washed with water until an acid reaction is no longer noticeable. The dried substance is then crystallised from acetic acid, and shows a melting-point of 112° C. Alcohol and ether can be used as crystallising agents, but are not so good, as the substance crystallised from them will still have a slight yellow colour. One would expect, from the analogy between this substance and the aromatic bodies, that a dinitro compound would be formed, yet such is not the case. The mononitrophenylbienylketone, in long needle-like crystals, is formed. The analysis of the substance is as follows:—

0.0893 gr. of the salt yielded 4.45 c.c. nitrogen, at a temperature of 21° C., and a pressure of 745 m.m.

	Found.	Theory for C ₁₁ H ₇ S ₂ O ₂ N.
Nitrogen	5.55	5.29

The results of this work show, once more, that compounds may be formed from the fat series which show decided characteristics of the aromatic series, and which may be regarded as belonging to it; also, the similarity between biophene, and thiophene, and benzol has been shown.

In conclusion, let me add that the action of phosphorus trisulphide upon thiodiglycolic acid has been tried, and a product obtained which shows the isatin reaction, proving that in all probability the dimethylbiophene or bioxene can also be obtained in the same manner as biophene.

On Muscarine and its Higher Homologues.—H. Lochert.—The author has obtained muscarine synthetically founded upon the total combination of trimethylamine and bromoacetal. He has also obtained compounds of bromoacetal with triethylamine, dimethylaniline, pyridine, and quinoline.—*Bull. de la Soc. Chim. de Paris*, Vol. iii., No. 12

INTERNATIONAL STANDARDS FOR THE
ANALYSIS OF IRON AND STEEL.*EXTRACTS FROM THE WORK OF THE AMERICAN COM-
MITTEE.

By JOHN W. LANGLEY.

In the summer of 1888 it was the fortune of the writer to present the subject of the desirability of establishing a set of samples of steel, which should be analysed with extreme care, in order that they might become standards to which scientific and commercial analyses of iron and steel could be subsequently referred. Also, that greater uniformity in the results of analyses might be brought about, since these standards would bear towards analytical methods somewhat the position which the original units of weight and length, the gramme and metre, or the pound and yard, preserved in Paris, London, and Washington, do to the mechanical arts.

The plan met with hearty co-operation, with the result that committees were appointed in Sweden, Germany, France, England, and America to receive the material and to see that the necessary analyses were executed.

In England the British Association for the Advancement of Science appointed a committee, who subsequently published a plan of operations for that country, reports of which will be found in the British Association Transactions for 1888 and 1889.

The writer of this paper was entrusted with the duty of preparing the material and distributing it to the five countries named. This has been done, and analytical work on the steel is now going forward.

In the United States a committee of seven chemists was appointed to make the analyses, consisting of:—Andrew A. Blair, Philadelphia, Pa.; Regis Chauvenet, Golden, Colorado; Thomas M. Drown, Boston, Mass.; Charles B. Dudley, Altoona, Pa.; John W. Langley, Pittsburgh, Pa.; Albert B. Prescott, Ann Arbor, Mich.; Porter W. Shimer, Easton, Pa.

This committee held a meeting at Washington, Feb. 19th, 1890, and came to the decision that the whole subject of the existing methods for the determination of carbon in iron and steel seemed to be affected by so many discrepancies and differences of opinion that, before beginning work on the International Standards, it would be desirable to make a preliminary study of methods. Accordingly, the writer was asked to prepare some additional material which could be used in somewhat large quantities for the above purpose only, and which should be known as the "Experimental Standards," to distinguish them from the "International" ones.

Method of Making the Exp. Standards.

An ingot of tool steel, $3\frac{1}{2}$ inches square, poured from a single crucible in which the metal had been thoroughly "dead melted," was heated and hammered barely enough to round off the corners. The ingot was then cut into two pieces, one of which was then re-heated and hammered down to a bar $1\frac{1}{2} \times \frac{1}{2}$ inches. The other half of the ingot was turned in a lathe with a blunt tool, exactly as in the manufacture of the International Standards, and the turnings, after sifting from fine dust, were thoroughly mixed and then sealed up in glass jars. The hammered bar was drilled and the drillings similarly treated. This material was given by the Crescent Steel Company, of Pittsburgh.

The object of this was to have two bodies of metal presumably identical in original composition, but one of which had received a large amount of mechanical work, the other approximately none. These samples are designated Exp. Standard, Ingot, and Exp. Standard, hammered, respectively.

Scope of the Proposed Work.

The committee decided to limit the investigation to the following points at first:—

a. The best method of conducting the igneous combustion of the carbon previously liberated from the metal by a solvent.

b. The best method of conducting the aqueous combustion of the carbonaceous residuum left by the solvent.

c. The influence of the solvent on the quantity and mode of release of the carbon.

For division a it was decided further to commence with a study of the method of burning the carbon in a stream of oxygen.

This work was assigned to Messrs. Blair, Dudley, and Shimer.

For b. The examination of oxidation methods by hot solutions of sulphuric and chromic acids. Work by Mr. Langley.

For c. The use of a double chloride of copper and ammonium, or of copper and potassium, either neutral or acid. Work by Messrs. Blair and Dudley.

A description of the apparatus for igneous combustions is as follows:—

The apparatus used by Dudley consisted of an ordinary Bunsen furnace with 15 burners, in which was a porcelain combustion tube five-eighths of an inch internal diameter, and eighteen inches long. Inside this tube, about three inches from the end towards the absorption apparatus, was granulated and porous oxide of copper, occupying about four inches of the length of the tube, and filling the bore. This was held in place by asbestos plugs at either end. Next to the oxide of copper, towards the boat, was placed a roll of metallic silver about 4 inches long, nearly filling the bore of the tube. Rubber corks were used at each end. The combustions were all made in oxygen gas, using air to finish the aspiration and clean out the tube. The oxygen gas used was obtained in the market in cylinders, the gas being compressed to 250 lbs. per square inch. Between the oxygen holder and the combustion tube was placed first a copper tube, about four feet long and $\frac{1}{2}$ inch in diameter, fitted with three coils at the middle; next a potash bulb, and after that a chloride of calcium tube. All the oxygen gas, and the air used in the combustions, was passed through these parts. The copper coils were kept red-hot by a Bunsen burner, during the passage of the gases, the idea being to burn any possible traces of combustible in the gas or air, and absorb the CO_2 formed before they should go into the combustion tube. Between the absorption end of the combustion tube and the potash bulbs were, first, a washing tube containing about 5 c.c. of sulphate of silver solution with perhaps $\frac{1}{2}$ gm. of silver sulphate, and next, a chloride of calcium tube. The potash bulbs were of the Geissler form, of small size made to order. These were fitted with a small chloride of calcium tube containing chloride of calcium simply, and commonly called the prolong. The whole absorption apparatus weighed, when charged, about 60 grms. The absorbing solution in the bulbs was the ordinary caustic potash solution recommended by Fresenius. The absorption apparatus was protected against the aspirator bottle by a full size chloride of calcium tube. The joints were made with ordinary rubber tubing. The carbon from the steel was caught on an asbestos filter in a platinum boat, and dried after very complete washing at about 90°C . The boat with its filter and carbon was put into the tubes without transfer. During combustions a slight pressure above the atmosphere was always maintained in the combustion tube. Careful experiments show that the sulphate of silver washing tube is a complete protection against hydrochloric acid, and the metallic silver in the tube was relied on for protection against free chlorine, or other chlorine compounds. The time of making a combustion was about an hour and a quarter; fifteen to twenty minutes being taken to heat the oxide of copper, about half an hour for the burning, and twenty-five to thirty minutes for the air aspira-

* Transactions of the American Institute of Mining Engineers, Pittsburgh International Session, October, 1890.

tion. Blair's apparatus is substantially the same as the above. His purifying train following the combustion tube contains a tube of anhydrous sulphate of copper on pumice stone. This tube is always freshly filled.

Shimer's apparatus is a porcelain tube containing oxide of copper. A stream of purified oxygen is used. An anhydrous copper sulphate absorbing tube is employed, and then the customary CaCl_2KHO and CaCl_2 absorbents.

Preliminary Results of Oxygen Combustion.

In the following analysis, a solution of double chloride of copper and ammonium, except where otherwise noted, was used as the solvent of the steel. The carbon sponge was washed with dilute HCl and water till the filtrate was free from chlorine, then the asbestos with adhering carbon was put into the combustion tube. These determinations were made before the elements of uncertainty attaching to the use of double chloride were discovered, and it will be seen in the latter part of this paper, that quite different numbers can be obtained.

Under date of April 22nd, 1890, Dudley reports: Exp. Standard, Ingot, contains:—

Carbon	1'058 per cent.
"	1'065 "
"	1'052 "
"	1'058 "

Average .. 1'058 per cent.

Ditto hammered standard:—

Carbon	1'050 per cent.
"	1'051 "
"	1'051 "
"	1'060 "
"	1'050 "
"	1'056 "
"	1'056 "

Average .. 1'053 per cent.

Under date of April 5th, 1890, Blair reports, that using double chloride of copper and ammonium, with enough ammonia added to produce a slight cloud, and re-dissolving the basic salts formed in acidulated double chloride, he obtains:—

	Ingot.	Hammered.
Carbon	1'016	1'022 per cent.
"	1'013	1'020 "
"	1'015	1'025 "
"	1'010	1'022 "

He then weighed out four portions of the "ingot" sample, and added to each 200 c.c. double chloride of copper and ammonium, after adding to each the following amounts of strong HCl :—

HCl .	Carbon.
10 c.c.	1'048 per cent.
20 "	1'048 "
30 "	1'048 "
40 "	1'051 "

He then took four portions of the "hammered" sample, and treated them each with 200 c.c. of double chloride and 20 c.c. HCl . Results:—

Carbon	1'046 per cent.
"	1'046 "
"	1'044 "
"	1'049 "

Showing that the addition of HCl in excess of five per cent does not sensibly vary the results.

A combustion of sugar at the same time showed:—

Carbon	42'05 per cent.
"	42'14 "
Theory	42'11 "

In answer to the suggestion that possibly oxides of nitrogen might be derived from the breaking up of am-

monia retained by the carbon sponge, Blair reports, under date of April 17th, that he has made four combustions on the "ingot" sample, using a four times re-crystallised double chloride of copper and potassium.

No. 1, Carbon	1'010 per cent.
" 2, "	1'044 "
" 3, "	1'012 "
" 4, "	1'022 "

No. 1 was dissolved in the filtered solution of the above double chloride.

No. 2 was dissolved in 200 c.c. double chloride, with 200 c.c. strong HCl .

Nos. 3 and 4 were dissolved in the filtered double chloride, to which enough potassic hydrate had been added to produce a slight permanent precipitate.

Blair offers the hypothesis that a strictly neutral or slightly alkaline double chloride dissolves a small portion of the carbonaceous matter, which is consequently lost so far as the combustion is concerned. Therefore, the addition of acid, by preventing this action of the liquid on the carbon sponge, will give higher and more nearly accurate results.

That the use of an acid double chloride solution gives higher results was promptly verified by Dudley and Langley. This subject is more fully discussed in the latter portion of this paper.

Shimer reports, April 25th, that by using 4 grms. of steel in a neutral solution of double chloride of copper and ammonium, he obtains:—

"Ingot," average of two combustions, 1'055 per cent.

"Hammered," average of two combustions, 1'052 per cent.

The Wet Method.

The chromic acid combustion was conducted in an apparatus originally designed by Dr. Hermann Wedding, although the method of absorption used by him has been radically modified. Wedding's design consists of a flask capable of holding 220 c.c., and provided with a glass cap of two tubulures; through one of these passes a funnel tube with stop-cock, and through the other the delivery tube surrounded by a water jacket. All the joints are of ground glass.

The merit of this apparatus is its compactness and its freedom from rubber or cork joints, at least in the parts liable to come in contact with chromic acid. The absorption train, which is wholly different from Wedding's, consists of:—

1st. A tube filled with pumice stone and anhydrous sulphate of copper.

2nd. A small washing bottle containing the "pyro" solution referred to later on.

3rd. A solution of sulphate of silver.

4th. A wash bottle of strong sulphuric acid.

5th. A chloride of calcium tube, having a small plug of moist cotton in its anterior end.

6th. A Liebig tube, containing potassic hydrate solution.

7th. A U-tube, having solid potassic hydrate in its anterior limb and granulated calcium chloride in the posterior one.

8th. A chloride of calcium guard tube.

9th. An aspirator filled with water.

The absorption portion for CO_2 is constituted by Nos. 6 and 7. The other parts, except Nos. 2 and 3, need no explanation, since they are well known adjuncts of the chromic acid method described in such treatises on analysis as those of Fresenius and of Blair.

The method of conducting a combustion is to place the carbon, which has been liberated from 3 grms. of steel by the action of 150 c.c. of solution of double chloride of copper and ammonium, to which 10 c.c. of HCl has been added, into the flask, and run in through the funnel tube 100 c.c. of a solution made by dissolving 10'5 grms. CO_2 , 66 c.c. H_2O in 210 c.c. strong H_2SO_4 . Purified air is drawn through at the end of the combustion.

The train at first used did not contain the "pyro" tube

No. 2; under these conditions the following numbers were obtained from the exp. ingot standard:—

Carbon	1'099
"	1'145
"	1'040
"	1'058
"	1'109

A search was instituted to find the cause of these discordant results. It is well known that the carbon sponge from the action of the double chloride retains chlorine or hydrochloric acid in a form not removable by washing; suspicion at once fell upon the HCl known to be evolved from the carbon sponge.

A series of blank combustions were made, and also mixtures of air and HCl were drawn through the absorption train. It was found that the anhydrous CuSO_4 would only stop HCl when it was perfectly fresh and in relatively large quantity, a quite small degree of hydration impairing its absorbing powers seriously. A tube containing an aqueous solution of sulphate of silver was then added to the CuSO_4 tube, with the result that vapours of HCl are perfectly and completely arrested. When this point was established blank combustions were made and small quantities of chlorides introduced into the chromic acid mixture; it was invariably found that the potash bulbs gained in weight. As one example out of many the following is quoted:—

One tenth grm. of NaCl in generating flask. CuSO_4 and Ag_2SO_4 absorbents were interposed. The silver solution showed not a trace of chloride, and yet the potash train gained 0'0055 grm.

This gain appears to be owing to chloro-chromic anhydride, or to oxides of chlorine, not absorbable by copper or silver sulphates.

This observation is not new, for it has previously been noted by other chemists that chloro-chromic anhydride was not arrested by copper sulphate.

After a long series of experiments an absorbent for these bodies has been found in the following solution:—

Pyrogalllic acid	0'2 grm.
Potassic oxalate	5'0 "
Sodic chloride	3'0 "
Sulphuric acid	0'2 "
Water to make up to	20'0 c.c.

The theory of the action of this mixture is as follows:—

The pyrogalllic and oxalic acids are deoxidants. The sulphuric acid will form potassic sulphate, liberating a very little free oxalic acid to guard against the solution becoming alkaline. The sodium chloride is not essential, but it is advantageous by diminishing the solubility of CO_2 in the liquid.

The action of this absorbent is very energetic. It will allow HCl to pass through it without change, but the smallest traces of free chlorine, or of oxides of chlorine, or of chloro-chromic anhydride, at once turn the solution brown, and are either arrested or changed into HCl. Indeed, as a qualitative reagent this liquid will approximate to iodised starch paper.

In using this in the absorbing train, the copper sulphate tube may be dispensed with, the pyrogalllic liquid being used in its place, and followed by a sulphate of silver tube, so that the train between the generating flask and the potash bulbs will contain:—(1) a cooling tube; (2) the "pyro"; (3) the sulphate of silver; (4) sulphuric acid; (5) chloride of calcium.

Blank "combustions" were made as before with NaCl, using the Pyro train till it was proved that there was no systematic gain in weight of the potash bulbs.

As examples of carbon oxidation in presence of chlorides—Taken 0'0712 grm. sugar with a crystal of NaCl. Found 0'1098 grm. CO_2 . Theory 0'110 grm. Taken 0'030 grm. Ceylon graphite, of about 3 per cent ash. Found 0'0292 carbon, equal to 97'3 per cent carbon.

The following analyses were then made, using the new train:—

Exp. standard, hammered, 1'075 per cent C.	
" " " 1'070 "	
" " ingot, 1'041 "	
" " " 1'034 "	

It seemed possible that the carbon sponge left on the asbestos, after filtering from the double chloride solution, might suffer a slight oxidation and loss of carbon while drying. A set of duplicate analyses were therefore made on a variety of steels. The terms wet and dry, below, refer to the state of the carbon sponge when introduced into the chromic acid flask. The drying was performed at a temperature not above 100°C .

	Wet.	Dry.
Steel A	0'981	0'936 per cent C.
" B	0'836	0'813 "
" C	0'904	0'891 "
" D	1'054	1'073 "
" E	1'145	1'154 "
" F	1'095	1'108 "
" G	1'027	0'968 "
Pig	3'695	3'722 "
Totals,	10'737	10'665 "
Average,	1'342	1'333 "

These determinations were made before the discovery of the variability of action of double chloride with age and manner of crystallising, to be pointed out hereafter. Moreover, they were distributed over a period of three months, so that some of the differences may be properly attributed to the chlorides used. Still, these would pretty well neutralise each other in sixteen determinations, so that the practical identity of the final averages would appear to show that the sponges do not lose appreciable amounts of carbon by drying.

On the other hand, the "hammered" standard, similarly treated, but having the sponge dried in an air-bath at a temperature not exceeding 120°C ., gave—

	Wet.	Dry.
Carbon	1'064	1'027
"	1'059	1'023
"	1'064	1'018
"	1'045	1'032
Average	1'058	1'025

Apparently, therefore, there is a loss of carbon by drying the sponge at temperatures above 100°C . The same double chloride, acidulated, was used in these eight determinations.

(To be continued).

PHOSPHORUS IN PIG-IRON, STEEL, AND IRON ORE.*

By CLEMENS JONES, Hokendauqua, Pa.

THE analytical history of phosphorus in its relation to the metallurgy of iron is an interesting study, the progress of which runs parallel with the development of the greatest industry in the world. Without the means of finding out how much phosphorus crude pig-iron contained, the Bessemer steel process would have been impossible. To do this was originally tedious and slow work; on the other hand, the "direct" process of to-day, as well as the various special processes for steel or iron, have demanded the utmost rapidity in the operations of analytical chemistry.

In general, any rapid process for the conversion of un-

* Transactions of the American Institute of Mining Engineers, Washington Meeting, February, 1890.

refined metal into a product of standard composition depends upon the rapidity of some accurate means employed to control it. Moreover, in our modern practice, it is not improbable that the differences in physical properties among the various makes of iron or steel are affected, if not produced, by the use of different methods of analysis.

Recourse is always had for correction to the "standard methods," but I incline to think that these methods are susceptible to error. It is very certain that the system of duplicates would not be resorted to if the fact were otherwise. Even when duplicated, under the most careful and skilful manipulation, these standard methods produce disagreements. In proof of statements like these, which may sound heretical, I hope, further on, to cite some evidence worthy of attention. I do not now mean to lay claim to the distinction of discovering the ultimate corrective. That result will come, no doubt, in time, as the product of the experience of many workers.

In the case of phosphorus, as of the other ingredients of iron or steel, a great deal has been done to accommodate the methods of analysis in vogue to the growing necessity for more rapid procedures. Much of this work has concerned what might be called the incidents of method. There is no better example of the accumulation of these incidental improvements than the work done on phosphorus; and I believe that the final successful outcome of such progressive changes will be properly considered the standard method.

The ideal analysis, both for refined conditions and delicate determinations, is to be found in nearly all instances in a volumetric method. But in the preparatory stages the treatment by this standard method must consist of *visible reactions*.

I have classified what appear to be the salient features already embodied separately in the different methods; and when so related, they apparently fulfil the conditions and the object that each has had in view.

The method of Mr. F. A. Emmerton (*Trans.*, xv., 93), is the real beginning of this progressive series. As recommended, certain objections were found to it. The first of these was in the use of dilute nitric acid as a wash for the yellow precipitate. Acid ammonic nitrate, as suggested by Dr. Drown, was then substituted with only partial success. The presence of nitric acid in the final solution reduced for titration seriously interfered with accurate work. I communicated this fact to Mr. A. L. Colby, chemist to the Bethlehem Iron Co., who at the time was also experimenting. His conclusion, reached by careful examination through it, pointed out the remedy. I quote from Mr. Colby's notes, kindly placed at my disposal:—

NOTES ON EMMERTON'S METHOD FOR PHOSPHORUS,
OCTOBER, 1887.

Blank Phosphorus Determination.—A clean dry 16 oz. Erlenmeyer flask was washed twice with am. nitrate wash (NH_4NO_3 , 200 grms.; HNO_3 conc., 30 c.c.; H_2O , 2000 c.c.), pouring it on a filter, and draining the flask as much as possible each time; the paper was then washed twice with the wash and sucked dry; the stem of the funnel was rinsed off on the outside with water, and the funnel placed in the flask; paper punctured with platinum rod, and washed with dilute NH_4OH (1:4), about 30 c.c. being used; 5 grms. granulated zinc was added to the contents of the flask, and 80 to 90 c.c. H_2SO_4 of the dilution, 150 H_2SO_4 : 420 H_2O . A small funnel was put in the top of the flask, which was then heated till nearly all the zinc was dissolved. The reduced solution was then filtered; flask, funnel, and paper were thoroughly washed with hot water, and the solution was titrated with KMnO_4 at once.

A permanent tint was not obtained until 12 c.c. of KMnO_4 had been used. (As 1 c.c. of KMnO_4 = 0.000106 grms. P., this is equivalent to an error, in analysing an ore where 8 grms. are taken, of 0.016 per cent., and for a

steel or iron where 4 grms. are taken, of 0.032 per cent P.).

Above blank test, using as a wash HNO_3 (1:25). Permanent tint at 8.5 c.c. of KMnO_4 .

Above blank test, using as a wash HNO_3 (1:50, which Emmerton recommends). Permanent tint at 3.2 c.c. of KMnO_4 .

Above blank test, using as a wash H_2SO_4 (1:50). Permanent tint at 0.45 c.c. KMnO_4 .

Above blank test, using as a wash $(\text{NH}_4)_2\text{SO}_4$, made up as follows: $(\text{NH}_4)_2\text{SO}_4$, crystals, 25 grms.; H_2SO_4 , conc., 50 c.c.; H_2O , 2500 c.c.

Permanent tint at 0.45 c.c. of KMnO_4 .

Zinc 5 grms. and H_2SO_4 (90 c.c.), placed directly in a dry, clean flask, reduced as usual, filtered, washed and titrated. Permanent tint at 0.45 c.c. of KMnO_4 .

To ascertain if yellow precipitate is soluble in H_2SO_4 , or in $(\text{NH}_4)_2\text{SO}_4$ wash, which would prevent its use as a substitute for NH_4NO_3 wash. Selected crystals of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, containing by theory 8.6572 per cent P, were dissolved, 1.5408 grms. in 500 c.c. distilled water, and the following tests were made:—(See Table, next page).

As the blanks run both with H_2SO_4 wash (1:50) and with $(\text{NH}_4)_2\text{SO}_4$ wash used up 0.45 c.c. KMnO_4 instead of 0.5 c.c., as subtracted above, analyses Nos. 4, 10, and 11 should show 8.685 per cent instead of 8.668 P.

The above analyses, using 10 c.c., were made on too small a quantity of Na_2HPO_4 . Small variations in KMnO_4 make too large differences in per cent of P, 0.5 c.c., or one drop of KMnO_4 , being equal to 0.007 per cent P.

But the set of analyses shows that even strong H_2SO_4 (1:5) exercises no appreciable solvent action on yellow precipitate, and that $(\text{NH}_4)_2\text{SO}_4$ wash is rather better in agreement than H_2SO_4 (1:50).

As an example of the possibilities of the method when using the $(\text{NH}_4)_2\text{SO}_4$ wash for determination of small amounts of P, a solution of C.P. Fe_2Cl_6 was tested. Of this solution, which had been prepared from the filtrate from P determinations in pig-iron, by precipitation with NH_4OH , thorough washing, and solution in HCl , 25 c.c., containing about 2.5 grms. Fe, were precipitated for P as usual; the cloud of yellow precipitate was filtered off, washed with H_2SO_4 (1:50), dissolved, reduced, &c., as usual, titration giving only 0.75 c.c. KMnO_4 , which after zinc correction of 0.5 c.c., equalled 0.001 per cent phosphorus—a result not obtainable when using NH_4NO_3 wash.

In addition the following test of ores were made, using $(\text{NH}_4)_2\text{SO}_4$ wash for the volumetric determinations, and washing four times on the paper (instead of twice, to test the solvent action, if any), and twice in flask.

Sept. 23.—*Filtration by suction*, taking the usual precaution of draining flasks and funnels, and washing stem of funnel.

10 grms. of ore dissolved; $\frac{1}{100}$ taken for phosphorus..

P per cent.			
No. 1524	20.9 c.c. KMnO_4	= 0.027	} After deducting 0.5 c.c., cor- rection for Zn.
" 1525	14.8 c.c. "	= 0.020	
" 1526	7.6 c.c. "	= 0.010	

Sept. 28.—*Gravimetric determination* on 10 grms. ore, $\frac{1}{100}$ taken for phosphorus, using NH_4NO_3 wash, twice in funnel and twice in flask—other conditions as before, but making two precipitations of NH_4MgPO_4 before weighing as $\text{Mg}_2\text{P}_2\text{O}_7$.

		$\text{Mg}_2\text{P}_2\text{O}_7$.	P per cent.
No. 1524		0.0079	= 0.025
" 1525		0.0062	= 0.022
" 1526		0.0026	= 0.009

Mr. Colby's notes close with some additional tests which confirm the foregoing.

Concerning the use of acid ammonic sulphate, it is in-

Tests with Various Wash-Waters.

Date. 1887.	Test No.	Wash-water used on yellow precipitate.	Na ₂ HPO ₄ solu- tion taken, c.c.	K MnO ₄ used, c.c.	Correction for zinc.	Phosphorus per cent.
Sept. 20	1	Ammon. nitrate	10	27.4	0.5	9.252
" 20	2	"	10	26.7	0.5	9.012
" 20	3	Ammon. nitrate, and then washed twice with water to remove NH ₄ NO ₃	10	25.8	0.5	8.702
" 21	4	H ₂ SO ₄ (1:5)	10	25.7	0.5	8.668
				Zinc ran thro'.		
" 21	5	"	10	25.3	0.5	8.530
" 20	6	H ₂ SO ₄ (1:50)	25	64.6	0.5	8.8195
" 20	7	"	25	64.6	0.5	8.8195
" 21	8	"	10	25.0	0.5	8.42
" 21	9	"	10	24.9	0.5	8.39
" 21	10	(NH ₄) ₂ SO ₄	10	25.7	0.5	8.668
" 21	11	"	10	25.7	0.5	8.668

interesting to note that nearly a year later Mr. Porter W. Shimer, in a paper before the Institute (*Trans.*, xvii., 100), observes: "Sulphuric acid and ammonium sulphate completely take the place of nitric acid and ammonium nitrate."

In the same paper Mr. Shimer describes the use of potassium permanganate as an oxidising agent. This appears to be the next important detail. By means of it the complete oxidation of the phosphorus to ortho-phosphoric acid, as Dr. Drown puts it, is accomplished. This is indispensable, and cannot be omitted in the solution of pig-iron, steel, or iron-ore.

Dr. Drown's method (*Trans.*, xvii.) of dissolving pig-iron or steel in nitric acid of 1.135 specific gravity, in which potassium permanganate, as suggested by Mr. Shimer, is used as an oxidising agent, is a most happy expedient. It opens the way to the most rapid method in use. There is no ground to doubt its efficacy, if applied to iron ore, by taking advantage of a simple device, namely, solution in dilute sulphuric acid of the fused residue from the ore. According to Dr. Drown, silicon exerts no influence on the determination of phosphorus in pig-iron or steel. As a soluble silicate there is good evidence of its non-interference in the treatment of iron ore. A determination in iron ore can thus be made in nearly the same time as in iron or steel.

Here, then, seem to be collected nearly all of the requisite conditions. There is but one remaining—the reduction of the molybdic acid. I believe that this is fully covered by using the method discovered by me for reducing ferric solutions (*Trans.*, xvii., 411). I have found that it applies in all respects equally well to the complete and instantaneous reduction of molybdic acid.

It is possible then to reconstruct a method, based on these incidents, which should be peculiarly adapted to every demand for the rapid and accurate determination of phosphorus.

Before advancing so far, however, I propose to show with what degree of accuracy these principles may be employed, by giving the following results. These were obtained by the Emmerton method, modified by the use of ammonic sulphate in washing the yellow precipitate, and by the use of the reductor.

No. 3588.—Pig-Iron.			
Weight. grm.	KMnO ₄ . c	Correction. c.c.	Phosphorus. Per cent.
0.5000	18.67	0.03	0.447
0.5000	18.52	0.03	0.443

1 c.c. KMnO₄ = 0.00012 P.

No. 3980

	Phosphorus. Per cent.
No. 1, gravimetric	0.717
No. 2, volumetric	0.720

The following comparison is between this method (called "Reductor") applied to iron ore, and the Emmerton method of adding the zinc directly.

No. 4260.			
Weight taken. grms.		KMnO ₄ . c.c.	Phosphorus. Per cent.
A 1.9700	Emmerton	16.9—0.2	0.101
B 2.6078	"	20.0—0.2	0.091
C 2.8800	Reductor	22.15—0.05	0.092
D 3.0760	"	23.81—0.05	0.092

No. 4261.			
Weight taken. grms.		KMnO ₄ . c.c.	Phosphorus. Per cent.
A 1.6901	Emmerton	30.01—0.2	0.212
B 1.9439	"	34.5—0.2	0.211
C 1.9915	Reductor	36.9—0.05	0.222
D 1.9982	"	37.1—0.05	0.222

In the series following, carried through like the foregoing, potassium permanganate was used to oxidise the solutions. This was done carefully before adding the ammonia. The improvement is marked.

No. 3681.—Pig-Iron.			
Weight. Grms.	KMnO ₄ . c.c.	Correction. c.c.	Phosphorus. Per cent.
0.5025	2.83	0.05	0.066
0.5030	2.72	0.05	0.063

Determination by Mr. Shimer,
by his Mb-Mg method

0.064

The small amount of the sample necessitated the low weights, which in that measure affected the determination.

No. 3680.—Pig-Iron.			
Weight. Grm.	KMnO ₄ . c.c.	Correction. c.c.	Phosphorus. Per cent.
0.5000	26.39	0.05	0.6321
0.5000	26.4	0.05	0.6324

Determination by Mr. Shimer,
by his Mb-Mg method

0.615

No. 3682.—Pig-Iron.			
Weight. Grms.	KMnO ₄ . c.c.	Correction. c.c.	Phosphorus. Per cent.
0.2500	23.21	0.05	1.111
0.2500	23.21	0.05	1.111

Determination by Mr. Shimer, by
his "sulphuric acid" method

1.07

The conclusion to be drawn is not that the direct use of zinc always gives uniformly low results (by reason of the higher correction), but that the same errors are introduced, as I have pointed out in the case of the reduction of ferric solutions.

(To be continued)

ON THE
VARIATION OF THE DENSITY WITH
THE CONCENTRATION OF WEAK AQUEOUS
SOLUTIONS OF CERTAIN SALTS.*

By Prof. J. G. MacGREGOR, D.Sc.

In a paper on "The Density of Weak Aqueous Solutions of Certain Salts,"* which I had the honour of laying before the Royal Society of Canada in 1885, I pointed out, as an incidental result, that in the case of zinc and magnesium sulphates, the increase in density produced by adding the anhydrous salt to water was proportional, or very nearly proportional, to the amount of salt added, provided the solutions thus formed did not contain more than about 2 or 1 per cent respectively of salt. I have recently had occasion to make a number of determinations of the concentration and density of dilute solutions of the above salts and of several others, and to hunt out similar determinations by other observers; and the data thus obtained enable me to settle, in the case of a number of salts, the limits of concentration within which this simple proportionality holds.

The solutions which I examined myself were made by mixing weighed quantities of the crystallised salt with weighed quantities of water. The salts had been purchased as pure, and had been re-purified by crystallisation. The water had been carefully distilled. In the case of iron sulphate solutions it was boiled in order that the solutions employed might contain but little dissolved air.

In all cases at least two solutions of any one salt were prepared by mixing weighed quantities of the salt and of water. Usually the other solutions required were prepared by diluting one of these with water, or strengthening it by adding salt. In the case of iron sulphate, all the solutions used were prepared by mixing salt and water directly, this course being pursued in the case of this salt, because of the fact of its undergoing progressive decomposition after being dissolved in water, and of the consequent necessity of determining the density of a solution as soon as possible after the solution had been formed.

In preparing the solutions, all determinations of mass were made by the method of double weighing, and all weighings were made in stoppered bottles. The weighings were of course reduced to *vacuo*. The errors of the standards employed were neglected. The balance used was a delicate one made by Colliot, of Paris. In calculating the percentage of anhydrous salt in the various solutions, the values of the atomic weights given in Clarke's "Constants of Nature" were employed.

Densities were in all cases determined by means of a specific gravity bottle. The bottle used had a volume of about 50 c.c. It was of thin glass, but was not so thin as to be readily deformable, and was provided with an accurately ground perforated glass stopper. All determinations of density were made at 20° C. A bottle containing the solution and a thermometer was placed along with the specific gravity bottle in a bath slightly above 20° C. When the solution had taken the temperature of 20° it was at once poured into the specific gravity bottle, and the latter stoppered, dried, and weighed. The thermometer used had been provided with a table of corrections at Kew. Weighings for the determination of density were made in one pan only (always, of course, the same pan), the double weighings for the determination of mass having shown that the ratio of the lengths of the arms of the balance was practically constant. In calculating the densities from the observations, the usual corrections were applied.

In using the determinations of other observers, I found that in many cases they had not stated whether their published percentages were percentages of anhydrous or of crystallised salt in solution, and that in many cases

also they had omitted to state whether their specific gravities were referred to water at the same temperature as the solution, or to water at some other temperature as 0° C. or 4° C. In the former cases, however, comparison of the observations of different men usually showed whether anhydrous or crystallised salt was meant. In the latter it was often possible, especially when several observations of dilute solutions were given, to determine the temperature of the water which was taken as the standard substance by plotting a curve of concentrations against specific gravities, and noting the point of its intersection with the axis of specific gravities.

In the case of all salts for which the densities of sufficiently dilute solutions have been determined, either by myself or by other observers, I find that up to certain concentrations, varying from 1 to 5 per cent of anhydrous salt in solution, the excess of the density of a solution over that of water at the same temperature as the solution is directly proportional to the percentage of salt in the solution. In symbols, if D_t , d_t are the densities at the same temperature t of a solution and of water respectively, and if p is the percentage of anhydrous salt in the solution, we have thus—

$$D_t = d_t + k p,$$

where k is a constant for all sufficiently dilute solutions of any one salt. The value of the constant k for any one salt having been determined, the densities (in grms. per c.c.) obtained from the above formula, are found to agree with observed values to the fourth place of decimals within the limits of concentration specified above.

The following tables give the concentrations and observed densities of dilute solutions of a number of salts, together with the densities calculated by the aid of the above formula with the proper value of k . The fourth column gives the differences between the observed and calculated values. The values of the density of water used in these calculations are those given by Volkmann,* which are based on the observations of Hagen Matthiessen, Pierre, Kopp, and Jolly.

Zinc Sulphate.—ZnSO₄.

Observer:—The author.

Temperature:—20° C.

Formula:— $D_{20} = 0.99827 + 0.0103918 p$.

Percentage of anhydrous salt in solution.	Observed density at 20° C. Grms. per c.c.	Calculated density at 20° C. Grms. per c.c.	Difference.
1.1622	1.01032	1.01035	+0.00003
1.8698	1.01774	1.01770	-0.00004
2.7281	1.02662	1.02662	0.00000
5.9150	1.06104	1.05973	-0.00131

The above formula thus gives the densities of solutions of zinc sulphate accurately to four places of decimals, provided they do not contain more than about 3 per cent of anhydrous salt in solution.

Magnesium Sulphate.—MgSO₄.

Observer:—The author.

Temperature:—20° C.

Formula:— $D_{20} = 0.99827 + 0.0106324 p$.

Percentage of anhydrous salt in solution.	Observed density at 20° C. Grms. per c.c.	Calculated density at 20° C. Grms. per c.c.	Difference.
0.6907	1.00553	1.00561	+0.00008
1.6525	1.01584	1.01584	0.00000
2.5809	1.02525	1.02571	+0.00046
3.7689	1.03700	1.03834	+0.00134

The formula is thus applicable up to about 2 per cent. The following is another series of observations of solutions of the same salt:—

* From the *Trans. Roy. Soc. Canada*.
Ibid., vol. iii. (1885), sec. 3, p. 15.

* *Wied. Ann.*, xiv. (1891), p. 260.

Observer:—Schiff.*

Temperature:—23° C.

Formula:— $D_{23} = 0.99762 + 0.0098176 p$.

Percentage of anhydrous salt in solution.	Observed density at 23° C. Grms. per c.c.	Calculated density at 23° C. Grms. per c.c.	Difference.
0.4879	1.00241	1.00241	0.00000
0.9758	1.00720	1.00720	0.00000
1.4637	1.01199	1.01199	0.00000
2.4395	1.02176	1.02157	-0.00019

Thus in the case of Schiff's observations also, the formula holds up to between 2 and 2.5 per cent.

(To be continued).

NOTICES OF BOOKS.

The Chemistry of Iron and Steel-Making, and of their Practical Uses. By W. MATTIEU WILLIAMS, F.C.S., F.R.A.S. (formerly Chemist in the Works of Sir J. Brown and Co., Lim.). London: Chatto and Windus.

MR. WILLIAMS has produced several works both scientific and technical, as well as some of a more general nature. But, unlike some versatile authors whom we might name, he never comes forward to instruct the public on any subject without knowing something or other more about it than may be compiled from the literature of the day. He is not merely an acute observer, but one who can make his observations teach useful lessons. In his preface he divides working men into three great classes. The first, and unfortunately the largest, neither know, think, or care anything about the scientific basis of their work; the second treat the laboratory with contempt, and resent the interference of the chemist; the third class are awakening to a perception that practical men might after all "learn something from the theorists."

The present work is the completion of a few lectures which Mr. Williams delivered some years ago to an audience of this third section. He urges that the men of this class "crave to learn the why and the wherefore of the operations which they are daily performing. He protests against putting into the hands of such men a re-hash of mere scholastic treatises, and fears that forcing such matter upon them under the guise of technological instruction may drive the men back into the second class. He pleads for the scientific—not literary—education of the working man, so as to render him a better observer and more able to draw right conclusions from phenomena.

His introductory chapter is chiefly devoted to an account of the struggles of Dud Dudley, son of Edward, Lord Dudley. To him we are indebted for the reduction of iron ores with fossil fuel—a step greater than that effected by Messrs. Thomas and Gilchrist, since without it the English iron trade would be simply non-existent.

We are often told that by special good luck Britain is most abundantly supplied with coal and iron ores in immediate juxtaposition; but the author reminds us that our native iron ores are among the worst and the poorest in the world, and that the chief improvements in the manufacture of iron have been the result of struggles against the difficulties presented by impurities. He does not, however, consider that iron pyrites, even after its sulphur has been roasted out in the manufacture of sulphuric acid, has a future as an iron ore, though it may be useful as a source of certain salts of iron.

On the word "slag" the author entertains peculiar views. The vitrified matter which is run off from smelting furnaces he would name "cinder," and confine the term "slag" to the scales struck off from iron in forging. This proposal, if carried out, would, we fear, lead to confusion. "Cinder," except in iron-works, signifies coal

from which the hydrocarbons and all the more volatile matter has been burnt away, and which is thus converted into a kind of coke. But whatever we may agree to call the mixture of silicates run off down the furnace, its uses are not sufficiently numerous and extensive. The proposal to employ it as a raw material for coarse glass bottles seems, according to the author, not to have been successful. Slags rich in alumina and poor in lime, if dissolved in hydrochloric acid, form a crude aluminium chloride far superior to alum for the treatment of sewage and other foul waters.

The author's demand upon blast-furnaces is high, but not utopian. He writes: "Any blast-furnace which does not roast its own ores, coke all its own coal, and causticise its own lime, is an imperfect machine, with which the enterprising iron-master should continue to be dissatisfied." At the same time, if the blast-furnace cokes all its own coal, we fear that the ammonia and the tar with its bases will not be utilised. The same chapter concludes with a pithy hint to utilisers of waste materials. Where labour is dear and fuel abundant "the colliery proprietor who gets his coal at four shillings per ton and his labour at five shillings per day, is reasonably deaf and blind to scientific demonstration which shows how he may save a ton of coal at the cost of a day's labour."

The chapter headed "Fallacies Concerning Steel" is most instructive. Mr. Williams exposes the notion held even by men of repute that the differences between steel, wrought-iron, and cast-iron, "essentially depend upon differences in the proportion of carbon." It has been asserted that merchantable steel could be made from English pig-iron by simply stopping the "blow" before complete decarbonisation. Hence many inventors have been deluded. They have thought to produce steel by simply reducing the 3 or 4 per cent of carbon in cast iron down to 1 or 1½ per cent, quite forgetting the necessity of eliminating the phosphorus, sulphur, and silicon.

Another common and dangerous error has been to forget that metal of very high tenacity, as measured by the application of a strain gradually increasing, is able to bear a sudden shock. Hence mere tenacity, measured as above, is no proof of the suitability of a steel for girders, guns, armour plating, &c. The Tay Bridge had successfully borne the tests then in use, and had been pronounced satisfactory. But a comparatively slight vibration added to the strain of a tempest destroyed it in a moment. The author is of opinion that for rails, tyres, &c., mild steel is far superior to wrought-iron. But for boiler-plates, armour-plates, girders, angle-iron, &c., wrought-iron is superior.

The following remark is humorous:—"The spectro-scope is a wonderful instrument, one of its great merits being remarkable docility. An energetic man with a clearly defined theory before him appears to be able to discover in a well-constructed spectroscope whatever the theory demands."

We find a nobly indignant denunciation of the policy which equips our soldiers with brittle sabres and flexible bayonets. Why do we blame the ignorant public for buying "cheap and nasty" articles, when our authorities think it prudent to risk the life of trained soldiers—perhaps the loss of a campaign—in order to economise some fraction on a weapon?

We cannot, however, carry any further our examination of this most instructive book, which is, or should be, valuable to others besides metallurgists and engineers.

Practical Inorganic Chemistry—Analysis and Sketches. By E. J. Cox. London: Percival and Co.

THE author of this book is described on the title-page as head master of the "Technical Science School," Birmingham. If his work is to be taken as a fair index of the kind of teaching in this and similar institutions we can only say that the sooner they are abolished the better it will be for the progress of science in this country.

* *Ann. Chem. u. Pharm.*, cviii., p. 336; see also Watts' "Dictionary of Chemistry," Art. *Magnesium Sulphate*.

There is hardly a page in the book that does not show the author's want of practical knowledge of his subject. It will suffice to pick out a few of the most glaring examples from a list that would fill a column of this paper. On page 40, in the sketch illustrating the preparation of nitrous oxide, the gas is carefully dried by passing it over calcium chloride and is then collected *over water*! Sketch No. 21, again, on page 42, shows ammonia gas being collected at a pneumatic trough that must contain, at the lowest estimate, three hundred-weights of mercury (value about £40 sterling). It is evident from this—and, indeed, from the remarks on page 34—that the students are not intended to *perform* these experiments; that is a troublesome detail quite unnecessary for the object of the "Technical Science School," which is, of course, to get the maximum number of "passes" (with the minimum of trouble and knowledge) in the inevitable examinations. If we turn to the section on analysis we shall fare no better. On page 28 the student is directed to confirm the presence of calcium in a precipitate by dissolving it in HCl, and adding to separate portions of the solution ammonium oxalate and sodium phosphate. There is no hint of the necessity of first neutralising the acid; doubtless the author (who writes himself F.C.S.) prefers to let his students find out such details for themselves. On page 22 the method of testing for nitric acid given is to "*Boil well* with strong H_2SO_4 ," allow to cool, and then add ferrous sulphate. Has the author ever tried the experiment in this form, we wonder?

The statement (on page 6) that the fumes evolved on heating sulphates turn red litmus blue, may be charitably put down as a slip: but we have quoted enough to show that the book is a thoroughly bad one—a "cram book" of the worst type written by a man without an adequate knowledge of the subject he essays to teach. It is a standing reproach to the Science and Art Department, which unfortunately controls so much of the science teaching in this country, that it has taken no adequate means to put the teaching of science into the hands of really competent men. A step in the right direction has been taken within the last few years by raising the necessary qualification from a second-class to a first-class in the "advanced" stage; but it is to be hoped that this will not be considered a final settlement of the question.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, vol. lxii., p. 212, you published the circular-letter which has been sent round to the members of the Chemical Society by Messrs. Lloyd and Teed, and from which it seems they are desirous of inducing the Fellows to ignore the objects for which the Society was founded—viz., "the promotion of chemistry and of those branches of science immediately connected with it," or, as the Charter puts, "for the general advancement of chemical science,"—and to transform it into an eclectic body, which should only admit those who have "scientific claims," whatever that may mean, and thereby convert the Fellowship into a sort of Chemical Degree, or, as they express it, "The dignity of the Fellowship of the Chemical Society."

If this radical change were effected, it would have two results:—

1. As only a comparatively small number of the candidates for admission have attained any fame as scientific chemists, or, as Messrs. Lloyd and Teed put it, can advance "scientific claims," the number of Fellows would gradually become smaller, the income of the Society

would diminish, and the Council would be obliged to cut down the Journal, by omitting the Abstracts, and, possibly, also be unable to publish in full the original papers communicated to the Society.

2. The point to which I wish especially to draw attention, however, is that this is, whether designedly or not, a side attack on the Institute of Chemistry, which was intended by its founders to be *supplementary to the Chemical Society*, and is empowered by Royal Charter to grant certificates to those who are competent. The Fellowship of the Chemical Society neither is, nor is intended to be, evidence of an advanced knowledge in chemistry; on the other hand, the Fellowship of the Institute is recognised by the Government, as the following letter, recently addressed to the President, Dr. James Bell, will show:—

"SIR,—I am directed by the Local Government Board to advert to your letter of the 30th July last, and, in reply to state that they have already been in the habit of accepting the Fellowship of the Institute of Chemistry of Great Britain and Ireland as adequate evidence of a knowledge of analytical chemistry on the part of a person to be appointed as public analyst.

I am, Sir,
Your Obedient Servant,

EDMUND W. WODEHOUSE,
Assistant Secretary."

It is hard to guess whether this attack is intended mainly for the purpose of injuring the Chemical Society, or is made with the object of hampering the Institute of Chemistry in its endeavour to raise the *status* of the professional chemist, or is simply an outcome of the mania for change which seems to be epidemic just now. However that may be, its most immediate and important result, if successful, would be to enormously increase the commercial value of the letters F.C.S. for trade advertising purposes; and, although this may be greatly to the advantage of some few Fellows of the Society, I feel sure the larger number, those who love Science for its own sake, and not merely for what they can make out of it, would view any change which was likely to produce this effect with the strongest disfavour.—I am, &c.,

CHARLES E. GROVES,
Secretary to the Institute of Chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 14, October 6, 1890.

On a New Method for the Determination of Urea.—P. Miguel.—The author has formerly stated that in order to obtain the soluble ferment of urea by means of very active urophagous bacilli it was useful to add a little ammonium carbonate to the culture solutions. The sole object of this precaution was to render the medium strongly alkaline, so that these bacilli may easily grow in the liquid. In default of alkalinity the sowings generally remain sterile. But among the urophagous microbia many, especially the micrococci, can develop themselves in neutral or even acidulated broth. Many of these microorganisms grow exclusively at the bottom of the vessels, producing deposits more or less granular, which never interfere with the transparency of the liquid, but charge it with a considerable quantity of a soluble ferment. Such liquids of a high degree of transparency should be chosen by preference for the determination of urea. If it is merely required to determine urea dissolved in pure water the operation is of the greatest simplicity. The diastaseiferous broth and the solution of urea are mixed in equal volumes. An alkalimetric determination is immediately made, and

the mixture is kept for two hours at 50° in a vessel very nearly full and fitted with a ground glass stopper. At the end of this time a second alkalimetric determination shows the quantity of ammonium carbonate which has been produced, and in consequence the weight of urea originally contained in the solution. If the liquid in which the urea has to be determined is urine or any organic liquid it is well, in order to avoid error from the absorption of ammonia by acids, acid salts, or from the formation of double ammonical salts, to treat the liquid in heat with a slight excess of ammonium carbonate. The liquid when cold is filtered if needful, and treated like the solution of urea in pure water. This method admits of great precision. If the weight of urea in a liquid reaches 10 per cent—at which proportion it becomes poisonous to the ferment—it is diluted with pure water. Sodium chloride in slight proportions, uric acid, ammoniacal and alkaline salts, extractive principles, albumen, and sugar in very large quantities do not interfere, which is far from being the case when urea is determined as nitrogen gas. Certain substances do interfere, as the author will explain in a future paper.

Experiments on the Cultivation of Wheat in a Barren Quartz Sand.—M. Pagnoul.—Phosphates, especially if soluble, play a capital part in the production of wheat. A mean yield of 46 quintals per hectare with a complete manure falls to 12 on the omission of soluble phosphoric acid, and to 2 if phosphoric acid is totally absent. The absence of nitrogen reduced the yield from 46 to 11. Potash is especially necessary if the nitrogen is supplied in the form of ammonia. The proportion of nitrogenous matter in the grain depends on the quantity of nitrogen supplied in the manure. It may fall to 8 per cent or rise to 20.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iii., No. 12.

Thermo-chemical Researches on Textile Fibres (Wood and Cotton).—M. Leo Vignon.—The substance of this paper has been already inserted.

Determination of Lead by Phosphomolybdic Acid.—Henry Beuf.—This determination may be effected either volumetrically or gravimetrically. In the former case the solution of lead is gradually treated at a boil with an aqueous solution of phosphomolybdic acid until the whole is precipitated, which is recognised by the yellow colour which the liquid takes as soon as it contains an excess of the liquid. This precipitation must be effected at a boil in order to obtain a dense precipitate, easy to wash and to filter. At lower temperatures the precipitate traverses the filter. It is let settle for a few moments, when the precipitate collects at the bottom of the vessel. It is washed by decantation with hot water, passing the washings through a tared filter. When the washing is completed the precipitate is put upon this filter, washed at 90–100°, and weighed. The quantity of lead is calculated by multiplying the weight of the precipitate by 0.54802. If the solution of lead before precipitation is acid it is neutralised with a solution of soda (not potassa or ammonia), and any precipitate which forms is re-dissolved in a few drops of acetic acid. By this method we obtain a precipitate containing less lead than do the sulphate and sulphide, whence the errors, if any, are smaller. For a volumetric determination the precipitation is effected as above; the precipitate is washed, and the washings are filtered through a common filter (not tared) taking care to let as little of the precipitate as possible fall on the filter. When the washing is completed the filter is perforated, and that portion of the precipitate which has collected upon the filter is washed into the vessel containing the principal portion. There are then added 10 c.c. of sulphuric acid and 2 to 3 grms. zinc. The whole is then gently boiled for an hour, when the liquid becomes brown. A solution of permanganate is then dropped in

with a burette until the liquid takes a permanent rose colour. As the permanganate has been standardised with a known quantity of a lead salt, the quantity of lead present is determined from the volume of permanganate consumed. The metals which interfere with this process are iron, copper, zinc, potassium, besides arsenic and ammonium. Iron is easily eliminated. When the liquor is neutralised with soda before precipitation an excess of alkali is used, which throws down the iron as ferric hydroxide, whilst the lead is re-dissolved. The iron is then removed by filtration. In presence of copper the lead is precipitated as if no other metal was present. A part of the copper is thrown down, but a washing with ammoniacal water dissolves the copper, whilst the lead remains insoluble. Potassium and ammonium are precipitated only in nitric solutions, but if they should be carried down they are easily removed by washing with ammonia. Zinc, as well as arseniates and arsenites, interfere with the precipitation. The compound of lead with phosphomolybdic acid is a dense white powder, insoluble in ammonia, soluble in potassa and soda, soluble in nitric acid even if dilute, but less soluble in acetic acid. One part of this compound dissolved in 500,000 parts of water. It contains 54.802 per cent of lead. For preparing the solution of phosphomolybdic acid the author takes the ammonium phosphomolybdate, a salt easily obtained, and treats it with *aqua regia* on the water bath until completely dissolved, and then evaporates to dryness. The acid thus obtained is dissolved in water and the solution is filtered. It suffers no change in keeping.

On Raoult's Ebullioscope.—R. Lespieau.—This paper requires the accompanying figure.

Action of Chloral upon Resorcine.—H. Causse.—By this reaction the author has obtained $C_{14}H_{12}O_6$ in colourless crystals, insoluble in water and benzene, but soluble in alcohol, ether, and alkaline lyes. The latter solutions in contact with air take a splendid fluorescence analogous to that of the phthaleine of resorcine. The author has further examined the behaviour of these crystals with acetic anhydride, the action of glyoxylic acid upon resorcine, and that of ethylic aldehyd upon pyrogallol.

On Bees'-Wax.—A. and P. Buisine.—The results show that bees'-wax has a composition which is approximately constant. The authors promise to give a method for the examination of commercial waxes and the detection of their falsifications.

Journal für Praktische Chemie.
New Series, Vol. xli., Part 8.

On the mixed Fatty-aromatic Ketones and their Oxidation of Potassium Permanganate.—Ad. Claus.—A first portion only of a memoir, which awaits its completion.

On Artificial Silver-Bismuth Glance.—R. Schneider.—The natural silver-bismuth glance, $Ag_2S \cdot Bi_2S_3$, occurs in a mine at Morococha in Peru. The author has obtained artificially a compound of identical composition.

On the Combustion Heats of some Organic Isomers.—Iw. Ossipoff.—This memoir does not admit of useful abstraction.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1615.

ON THE DETECTION AND SEPARATION OF MINUTE QUANTITIES OF HYDROGEN DIOXIDE AND OF URANIUM.*

By THOS. FAIRLEY, F.R.S.E.

VARIOUS authors have given 0.5 m.grm. as the smallest quantity of hydrogen dioxide which can be detected by the chromic acid test (Denigès, *Bull. Soc. Chim.*, 1890, p. 797).

The author has detected less than this quantity as follows:—To 5 c.c. of a 0.005 per cent solution of H_2O_2 in a test-tube, add 1 to 2 c.c. of ether, and then a small drop of chromic acid by means of a small pointed glass rod dipped in a 10 per cent solution of the acid. Shake up, and allow the ether to collect, when the blue due to the solution of the perchromic acid in ether is distinctly visible, especially against a white ground. If thought necessary, the yellow aqueous liquid can be screened from the eye by means of a sheet of paper held so as to leave the ether alone visible.

Now, 5 c.c. of a 0.005 per cent solution of H_2O_2 contain 0.25 m.grms. of H_2O_2 . Solutions more dilute, such as a 0.001 per cent solution of H_2O_2 , have in numerous experiments given negative results with chromic acid. By taking a smaller quantity than 5 c.c.—say, 1 c.c.—of a 0.01 per cent H_2O_2 , adding 1 c.c. of ether, and then a very small drop of the chromic acid solution, shaking up in a small test-tube, and allowing the ether to collect; the blue colour due to the perchromic acid is very distinct. In this manner 0.1 m.grm. H_2O_2 can be detected.

In 1877 (*Journ. Chem. Soc.*, pp. 1—24 and 125—143), the author made a careful study of many of the reactions of hydrogen dioxide, and described fully the preparation and properties of the uranium tetroxide. He has now endeavoured to apply the reaction between the salt of uranium and hydrogen dioxide to its detection in very dilute solutions or in very minute quantities. One advantage is that the dioxide can be collected as a precipitate, even out of a large volume of liquid, not too dilute to react with the uranium solution. In the absence of interfering agents (*Journ. Chem. Soc.*, 1877, p. 128), it affords a process of separation so that the dioxide can be estimated by weighing the uranium precipitate, or by titrating it with permanganate.

Dilute solutions of uranium nitrate and of hydrogen dioxide were prepared and their reactions observed. In each case, 5 c.c. of the uranium solution and 5 c.c. of the H_2O_2 solution was taken.

The Table shows that in very dilute solutions $\frac{1}{100}$ th to

$\frac{1}{100}$ th m.grm. H_2O_2 and $\frac{1}{10}$ to $\frac{1}{2}$ m.grm. of uranium can be detected by this reaction. Though the precipitates in experiments 7, 8, and 9 are very minute, weighing less than 1 m.grm., the turbidity in the liquid is well marked.

NOTE ON THE PREPARATION OF DIASTASE.

By J. ARTHUR WILSON

HAVING to make occasional estimations of starch by O'Sullivan's method, the following is the best way I have found of preparing diastase of the highest activity. 2 lbs. of the best malt are allowed to stand soaked in 10 per cent alcohol for eight hours, after which time it is pressed and filtered. The perfectly bright filtrate is then precipitated by absolute alcohol, till a milkiness ensues. It is then allowed to stand some time, decanted or filtered, and the precipitate washed once or twice with absolute alcohol.

The precipitate is then treated with cold water, filtered from the insoluble matter, and re-precipitated by alcohol. By repeating this treatment once or twice, and drying over phosphoric acid *in vacuo*, a white, easily soluble powder of high activity is produced.

Tottingham, Oct. 20, 1890.

INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.*

EXTRACTS FROM THE WORK OF THE AMERICAN COMMITTEE.

By JOHN W. LANGLEY

(Concluded from p. 220)

Mode of Release of Carbon.

In pursuance of the special work assigned to Dudley, in a study of the phenomena attending the release of the carbon from its connection with iron in the steel, some quite surprising results have been obtained. It is, perhaps, not too much to say that sufficient work has already been done to throw doubt on the accuracy of all recent carbon determination made with preliminary solution of the steel in double chloride of copper and ammonium.

Dudley began his study of this problem of the release of the carbon by quite an amount of preliminary study on the reliability of his apparatus and method of making combustions. A number of modifications were tried, but finally the apparatus and method previously described under the heading, Dudley's Apparatus and Method, were settled upon, and this apparatus and method were checked up by the following determinations:—

Into an ordinary glass combustion tube some 60 grms. of the well-known combustion mixture of chromate of

* Read before the British Association, Leeds Meeting, 1890 Section B.

* Transactions of the American Institute of Mining Engineers, Pittsburgh International Session, October, 1890.

No. of Experiment.	H_2O_2 per cent.	Ur nitrate. Per cent Ur.	Results.	Actual quantities used in m.grms.	
				H_2O_2 .	Ur.
1.	1.0	1.0	Immediate precipitate	50	50
2.	0.1	1.0	Precipitate in 30 seconds	5	50
3.	0.01	0.1	" 10 minutes	0.5	5
4.	0.01	0.01	" 4 hours	0.5	0.5
5.	0.005	0.05	" 30 minutes	0.25	2.5
6.	0.002	0.02	" 2 hours	0.1	1.0
7.	0.001	0.01	" 12 "	0.05	0.5
8.	0.001	0.01 + 5 c.c. pure alcohol	" 1 to 2 "	0.05	0.5
9.	0.0005	0.005 + 5 c.c. " "	" 12 "	0.025	0.25
10.	0.00025	0.0025	No precipitate with or without alcohol,	0.0125	0.125

lead and bichromate of potash were placed, taking care that the material did not reach to either end of the tube, and holding it in place at each end by asbestos plugs previously ignited. The tube was then placed in a furnace and a combustion made in the regular way, the position of the material, not reaching to either end, allowing the whole of it to be uniformly heated. This combustion was simply a blank to eliminate any possible error due to impurities in the combustion mixture. A small increase in weight in the absorption apparatus was found, and a second blank gave exactly the same results. This being done, three samples of three grms. each of the experimental standard ingot were treated with 200 c.c. each of the same double chloride solution rendered acid by 10 c.c. HCl. As this solution of double chloride will be referred to hereafter, we will say that it was made in Dudley's laboratory by obtaining from the market commercial chloride of copper and commercial chloride of ammonium, and dissolving these in water and mixing them in the proportions to form a double chloride containing one molecule each of the two salts. A small amount of free ammonia was added, enough to cause a perceptible separation of hydrated oxide of copper. The solution was then allowed to settle, and always filtered through previously ignited asbestos before using. This will be called solution "A." And it will be observed that the solution had not been crystallised. After solution was complete, the three tests were filtered into platinum boats, and three combustions made. Two of these combustions were made in glass tubes, using exactly the same amount of combustion mixture as in case of the blanks above described, and following the same manipulation, except that the boats with their carbon were buried in the combustion mixture in the tube. The third combustion was made in the apparatus, and by the method previously described under the head of Dudley's Apparatus and Method. The results obtained from these three combustions were as follows:—

	Per cent.
Combustion mixture No. 1, after allowing for blank, gave, carbon	1'102
Combustion mixture No. 2, after allowing for blank, gave, carbon	1'109
Combustion with Dudley's apparatus and method	1'106
Average	1'106

These results were regarded as showing that Dudley's apparatus and method gave fairly reliable results so far as the combustion was concerned.

But these results were confirmed by two further tests, as follows:—First—A direct combustion of crystallised and pulverised sugar in the same apparatus, and immediately following the last steel analysis above, gave,

Carbon	42'02 per cent.
Theoretical carbon in sugar	42'11 "

This was followed, secondly, by a blank combustion, everything being done exactly as in a regular combustion, except that nothing was put in the combustion tube. This blank showed a loss in the weight of the absorption apparatus of two-tenths of a m.grm.

The apparatus and method being regarded as satisfactory, attention was next given to the release of the carbon. Experiments were planned to demonstrate the effect of different states of dilution of the double chloride solution on the release of the carbon; also, to determine whether large or small amounts of double chloride solution changed results; and also to determine whether varying amounts of chloride of ammonium relative to the chloride of copper present produced any change. Before this part of the work was fairly entered on, however, a shipment of crystallised double chloride was obtained from the market. Since it had already been noticed in the work done on apparatus and method previously alluded to that discordant results were frequently obtained, it was at first

suspected that the apparatus and method were at fault, but after the tests of the apparatus, above given, were made, suspicion fell on the double chloride, and accordingly a nearly saturated solution was made from the shipment above alluded to. This solution will be called solution "B." Four combustions of the experimental standard ingot were made, using 200 c.c. of solution "B" rendered acid with 10 c.c. of HCl. These gave results as follows:—

No. 1	Carbon, 1'070
No. 2	" 1'067
No. 3	" 1'060
No. 4	" 1'065
Average	1'065

These results, it will be observed, are a trifle over 0'04 per cent lower than were obtained with the same steel, with the same apparatus and method, but using the uncrystallised double chloride solution "A." The problem at once arose how to reconcile these discrepancies. Obviously, if the apparatus and method could be trusted, either the solution "A" contributed to the absorption apparatus, which was weighed and counted as carbon, or solution "B" dissolved and carried off some of the carbon in the steel—or possibly both. Who could tell where the truth lay?

The first attempt to unravel the mystery consisted in taking 450 c.c. of solution "A" with 25 c.c. of HCl, and adding to it 1 grm. of steel. After the reaction was complete and the solution had been thoroughly mixed, it was filtered through asbestos. The result of this treatment was that this 450 c.c. of solution "A" had now in it some sub-chloride of copper, some chloride of iron, and also carbon liberated from steel had been floating around in it, affording an opportunity for any material which might be separated from the solutions by the reaction to attach itself and be filtered out. The reasoning was as follows:—If double chloride solution "A" contains any carbonaceous material in solution which separates when the solution is treated with steel, thus causing high results, a part, at least, of this material will separate when the 450 c.c. are treated with one grm. of steel, and be removed by the subsequent filtration, and consequently combustions made, using this treated double chloride solution "A," will show lower results. Two combustions were accordingly made of the experimental standard ingot, everything being exactly as in the previous combustions, except the use of the treated double chloride solution "A." These combustions gave:—

No. 1 Carbon	1'076 per cent.
" 2 "	1'070 "
Average	1'073 per cent.

Here was a reduction of a little over 0'03 per cent from the figures obtained using solution "A" untreated with steel, and the figures seem to indicate quite clearly that uncrystallised double chloride solution "A" contained something in solution that separated during the reaction with the steel, and gave erroneous and too high results.

In confirmation of this view, the following experiments were made: 200 c.c., the usual amount for a combustion, of solution "A" with 10 c.c. of acid, were treated with 5 grms. of experimental standard ingot, instead of 3; the assumption being, if there is a certain amount of carbonaceous matter in solution "A" which comes out during the reaction with the steel, lower results will be obtained if this error is divided over a larger amount of steel. Two combustions were made on this plan, which gave results as follows:—

No. 1 give Carbon	1'049 per cent.
" 2 " "	1'082 "
Average	1'065 per cent.

It is possible the first of these duplicates is a little low, as this carbon sponge from the larger amount of steel was a little difficult to manage in the boat; but as both the results are lower than those previously obtained from solution "A," it is evident they point in the direction that there is something in solution "A" that should not be there.

One more experiment was made on solution "A," as follows:—1000 c.c. of this solution was treated with 50 c.c. of HCl, and allowed to stand for some time. This solution was then filtered on the boat, and although nothing was visible to the eye, a combustion was made. The absorption apparatus showed an increase in weight of 34 m.grms. This corresponds to a trifle over 0.006 per cent of carbon in the steel which had been used in all the previous tests. This apparently indicates that although solution "A" probably contains something which it should not, that something only separates very slightly when the solution is treated with acid.

Thus far the evidence seems to point quite strongly in the direction that uncrystallised double chloride solution contains some carbonaceous matter which separates during the reaction with the steel. But who knows that crystallised double chloride does not also contain carbonaceous matter? And still further, who knows that either crystallised or uncrystallised double chloride does or does not dissolve some of the carbon of the steel during the reaction, and thus produce a loss?

Upon the first of these questions the following experiments were made:—450 c.c. of solution "B," which, it will be remembered, was made from crystallised double chloride obtained from the market, were treated with one grm. of steel and acid, as previously described for solution "A," and two combustions made. These two combustions gave:—

No. 1 Carbon	1.060 per cent.
" 2 "	1.061 "
Average	1.060 per cent.

These results are, it will be observed, only about 0.005 per cent lower than were obtained with the same solution untreated with steel, and seem to indicate that crystallisation removes at least the largest part of the carbonaceous material, such as was characteristic of solution "A." But the mother-liquor, from which the crystals forming solution "B" were obtained, may not have contained any large amounts of carbonaceous matter, and so the evidence seems most conclusive.

In continuation of this same study, four more combustions were made, two of them using solution "B," but no acid, and the other two likewise using solution "B" and no acid, but treating the solutions with steel, as previously described. These combustions showed as follows:—

	Untreated.	Treated.
No. 1 Carbon	1.036 per cent	1.030 per cent.
" 2 "	1.035 "	1.024 "
Average	1.035	1.027

These results show about 0.008 per cent lower for the treated double chloride than for the untreated, but the number of analyses and the number of samples of crystallised double chloride experimented on, seem hardly sufficient to set at rest the question as to whether crystallisation completely removes the probable difficulty due to carbonaceous matter in the mother-liquor.

Thinking that possibly carbonaceous matter might be introduced into the double chloride solution "A" by the commercial chloride of ammonium used in making it, four combustions were made, using some of the same shipment of chloride of copper alone which had been used in making solution "A." All four of the solutions had acid present, and two of them were made with the solution previously treated with one grm. of steel and filtered as already

described; the other two not treated. The same steel was used as in all the previous cases; these combustions gave the following results:—

	Untreated.	Treated.
No. 1 Carbon	1.072 per cent	1.040
" 2 "	1.056 "	1.050
Average	1.064	1.045

These figures, as will be observed, seem to indicate that part of the difficulty, at least, is due to the chloride of ammonium, since the chloride of copper alone gives nearly 0.04 per cent lower results than solution "A." They also seem to indicate that previous treatment with steel throws out something from even the chloride of copper alone. Too much importance should not, however, be attached to these results, as the reaction between the chloride of copper and the steel was very slow; and as acid was present, and it was impossible to keep the solution agitated continuously, it is probable a slight loss of carbon may have occurred. The variation in the duplicates may possibly be accounted for in this way.

Up to this point the evidence obtained seems to indicate:—1st, that uncrystallised double chloride made from commercial materials probably contains carbonaceous matter in solution; 2nd, that this may come partly from the chloride of copper, and partly from the chloride of ammonium; and 3rd, that crystallisation is probably advantageous in diminishing, if not completely removing, this difficulty. But some points are not quite certain, and accordingly the following experiments were undertaken to throw as much light as possible on the subject.

Commercial chloride of copper and commercial chloride of ammonium were obtained from the market. These were dissolved in hot water and mixed in the proportions to give a salt containing one molecule each of the two chlorides. On cooling the hot solution to a low temperature a large crop of crystals of the double salt was obtained. The mother-liquor was drained off from these crystals and set aside. Also a portion of the crystals obtained were rinsed with pure water and set aside. The remainder of the crop of crystals was again dissolved in hot water, evaporated a little, and cooled, giving a second crop of crystals, from which the second mother-liquor was drained off; they were then rinsed with pure water. The first and second crop of crystals were then each dissolved in water, forming nearly saturated solutions at ordinary temperatures. This gave three solutions to work with, viz.:—(1) The mother-liquor from the first crop of crystals, (2) a solution of the first crop of crystals, and (3) a solution of the second crop of crystals. In other words, solutions of uncrystallised, once crystallised, and twice crystallised double chloride. The mother-liquor solution was treated with ammonia sufficient to give a slight precipitation, and then filtered through asbestos. It was then divided into two parts, and one part treated with HCl to the amount of 5 per cent. The part treated with ammonia alone we will call basic mother-liquor and the other acid mother-liquor. Three combustions each were made with these two solutions, using the same steel and everything else as previously described. The results obtained were as follows:—

	Basic Mother-liquor. Per cent.	Acid Mother-liquor. Per cent.
No. 1 Carbon	1.086	1.145
" 2 "	1.081	1.130
" 3 "	1.067	1.150
Averages	1.078	1.142

Two results are quite noticeable in these figures:—1st, The acid mother-liquor gives higher results than any previous determination; and, 2nd. The differences between the basic and acid solutions is greater than in any previous case.

The second solution, viz., that from the first crop of crystals, was divided into two unequal parts. The

smaller of these was treated with ammonia and filtered as previously described, forming what we will call basic first crystals. The other part was filtered through asbestos and divided into two parts, one of which was treated with acid, as above described, and will be called acid first crystals. The other part was left without further treatment, and will be called neutral first crystals.

Three combustions each were made with these three solutions, showing as follows:—

	Basic First Crystals. Per cent.	Neutral First Crystals. Per cent.	Acid First Crystals. Per cent.
No. 1 Carbon	1.026	1.029	1.070
" 2 "	1.017	1.034	1.081
" 3 "	1.031	1.029	1.082
Average ..	1.027	1.031	1.077

The marked diminution in the amount of carbon between the mother-liquor and the first crop of crystals is very noticeable. In the basic results the difference is 0.051 per cent, and in the acid results the difference is 0.065 per cent. It will also be observed that there is a slight difference between the basic and neutral.

With the second crop of crystals only basic and acid combustions were made, the solutions being obtained as previously described. The results obtained were as follows:—

	Basic Second Crystals.	Acid Second Crystals.
No. 1 Carbon	1.016	1.049
" 2 "	1.028	1.056
" 3 "	1.023	1.052
Average ..	1.023	1.052

These results, taken in connection with what precedes, are, to our minds, exceedingly interesting. The marked diminution in the amount of carbon obtained with the second crystals over the mother-liquor, especially in the acid solutions, cannot fail to be noticed, and this would seem to indicate that double chloride made from commercial materials without crystallisation contains carbonaceous matter. This point would seem to be settled if it were not for the doubt whether the double chloride does not dissolve some of the separated carbon. Upon this point no positive data have yet been obtained. Two points further seem worthy of note. (1st.) The basic first and second crop of crystals give practically the same results, while the acids do not. And (2nd.) The farther away from the mother-liquor, the nearer the results from the basic and acid treatment come together. To our minds these facts, together with what precedes, seem to indicate that possibly the commercial material contains dissolved cellulose, and that crystallisation diminishes the amount of this, so that with the material used in the above experiments, once crystallising diminished the amount of cellulose, so that the basic liquid retained in solution what was left, since alkaline oxide of copper is a well-known solvent of cellulose, while the acid solution, even of the twice crystallised salt, still gives up a little cellulose to the carbon sponge.

In the special ground covered by Dudley in a study of the release of the carbon, the results of which are given quite at length above, the services of Dudley's principal assistant, Mr. F. N. Pease, have been found of the greatest value. He made all the combustions, and his suggestions have been most pertinent and useful.

A few attempts have been made to estimate the carbon in the Ex. Standards by methods not employing double chlorides, but with not much success.

Langley had proposed dissolving the steel in a hot solution of copper sulphate made as nearly neutral as possible, then filtering and burning the mixed copper and carbon sponge in oxygen. (*American Association Advancement of Science*, vol. xxiv., 1875.)

This method occasionally gives too low results, because

of the impossibility of being sure that the last particles of steel are dissolved. Dudley made the following trials on the Ingot Standard.

CuSO₄ was ignited to remove possible organic matter, then dissolved and filtered. The solution was made as neutral as possible, and allowed to stand on the steel several days. Result:—

Carbon.. .. 1.011 per cent.
" 0.972 "

Then to 300 c.c. of the sulphate solution was added 15 c.c. HCl. The attack of the steel was rapid, but some gas was evolved. Result:—

Carbon.. .. 1.002 per cent.
" 1.036 "
" 1.040 "

He then tried attacking the steel by solid silver chloride under water, and burning the silver and carbon sponge. Result on Hammered Standard:—

Carbon.. .. 0.796 per cent.

Langley made two determinations by putting the steel directly into the chromic-sulphuric acid mixture, without previous treatment by chlorides. Result on Hammered Standard:—

Carbon.. .. 0.788 per cent.
" 0.790 "

In this case more gas was evolved than what corresponded to the CO₂. It was found that methane would pass through the boiling chromic mixture without sensible oxidation; therefore, some of the carbon of the steel may have escaped in union with hydrogen.

Summary.

The conclusions here presented are not those of the committee in their official capacity. They are the views provisionally held by the members whose work is given above.

1. The combustion of carbon in a porcelain tube in a stream of purified oxygen, when the precautions indicated are used, gives sensibly accurate results.

2. If the carbon contains chlorine it is desirable to use a coil of metallic silver in the combustion tube, and it is apparently also *essential* to use some solution of silver, preferably the sulphate, in the purifying train.

3. The chromic acid method is capable of burning all the carbon used. If this carbon also contains chlorine, then it is *essential* to use some deoxidant in the purifying train, preferably pyrogallol acid with oxalate of potash; also a liquid silver absorbent must follow the deoxidising tube. Under these conditions this method gives sensibly accurate results.

4. The use of a small quantity of HCl in a solution of the double chloride of copper and ammonium invariably gives higher results than when a neutral solution is employed.

5. There is no evidence that the substitution of KCl for NH₄Cl in the double chloride is of any advantage.

6. The most important discovery made by the committee in this work pertains to the variable action of the double chloride solutions. This apparently throws doubts on the reliability of all carbon determinations previously made by this reagent, since they show variations on the same steel lying between 1.016 and 1.150.

When the degree of acidity is kept constant, the apparent quantity of carbon found is affected by the mode of preparation of the double chloride, by its age, and by the number of times it has been crystallised.

7. A carbon sponge derived from a double chloride solution does not appear to lose any carbon by drying at a temperature under 100° C., but loses if the heat is higher. The problems now before the committee, as suggested by the above results, are:—The determination of carbon in steel by some direct process not involving the use of double chloride; the direct combustion of finely divided

metal in oxygen or chromic acid is one of these, or by fusion in a mixture of bisulphate and bichromate of potash.

The determination, if possible, whether a neutral or alkaline double chloride liquid may not dissolve a portion of the carbonaceous residuum, and thus lead to results which are too low.

The determination whether the addition of acid simply prevents this tendency, or whether the use of acid may not favour the separation of pre-existing organic matter in the liquid, and its retention by the carbon sponge, thus leading to results which are too high.

The investigation of the cause of the influence of repeated crystallisations of the double chloride on the apparent quantity of carbon.

Finally, it is to be presumed that many, if not all of the above points, have attracted the attention of other analysts: and the committee will be glad to learn of the results and experience of others along these lines.

PHOSPHORUS IN PIG-IRON, STEEL, AND IRON ORE.*

By CLEMENS JONES, Hokendauqua, Pa.

(Concluded from p. 222).

Mr. Emmerton remarks that the "port-wine" colour is evidence of only incipient oxidation. On the contrary, this oxidation is very appreciable. It is only otherwise (*i.e.*, the molybdous acid oxidises slowly), as shown by Wernecke, when completely reduced.

The colour of these solutions, as ordinarily diluted, is always olive-green. By using the reductor this colour is invariably obtained. The following result from a piece of iron shows that it is applicable to very high phosphorus iron:

Weight. Grms.	KMnO ₄ . C.c.	Correction. C.c.	Phosphorus. Per cent.
0.5033	177.35	0.05	4.227

The colour of this solution was almost opaque until diluted. It was reduced instantly.

Dr. Drown's method I have found capable of being modified to great advantage. A large number of trials were made in strict accordance with the method as described, but neither the organic salts nor the acids gave acceptable results. Suspecting the trouble to lie in the use of these I substituted ferrous sulphate, which has the advantage of dissolving the manganic oxide immediately and being simultaneously oxidised. But the drawback to its use was that a correction for phosphorus had to be applied. None of the samples of ferrous sulphate received from a number of sources as "strictly C.P." were even low in phosphorus.

Messrs. Baker and Adamson, of Easton, Pa., kindly offered to experiment, and have succeeded in making the salt free from phosphorus. This was used in all of the determinations following.

The temperature of 90° C. was also found to be too high, molybdic acid precipitating in consequence. By adhering to 85° C., as recommended by Mr. Emmerton, this was overcome. Certain irons, high in manganese or fine graphite, cannot be easily oxidised before filtration. It is advisable always to test the solution with a few drops of KMnO₄ before adding the molybdate solution.

The method for pig-iron and steel now stands as follows:—

Dissolve in nitric acid of 1.135 specific gravity, according to Dr. Drown; allow the solution to boil one minute, then add the solution of potassium permanganate; after MnO₂ appears add a few small crystals of ferrous sulphate. Filter solution into flask; add sufficient NH₄OH

(0.90 specific gravity); when solution clears up add a few drops of KMnO₄, to insure oxidation, again dissolving if necessary. At 85° C. add to the solution 75 c.c. ammoniac molybdate solution (Dr. Drown's formula), and agitate violently for five minutes. Filter in Bunsen filter-flask, and wash thoroughly with ammoniac sulphate, observing all the precautions indicated by Mr. Colby. Dissolve the yellow phospho-molybdate in ammonia (0.96 specific gravity), *without* puncturing paper; wash once or twice with water, suck dry, and remove flask and stopper to suitable bell-glass. Pour the ammonia solution into small beaker, washing out flask with water three times. Place this flask under the bell-jar, and again filter the ammonia solution into it, this time washing paper thoroughly with water. Wash the zinc in the reductor, as required for ferric solutions; then add 30 c.c. to 50 c.c. sulphuric acid (1.32 specific gravity) to the ammoniacal solution, and filter through the reductor by strong suction, washing the same as indicated for ferric solutions and titrate as usual. The correction for zinc is obtained as described. I have made determinations in this way in half-an-hour. The following results were obtained in the above manner:—

The first is a "standard steel" which has been repeatedly tried by various chemists. The phosphorus is considered to be between 0.064 and 0.065. Below is a table giving the former results and the methods employed, the chemists being indicated by letters.

No. 4768.—Standard Steel.			
Chemist.	Phosphorus. Per cent.	Method.	
A	0.063	Emmerton.	
"	0.064	"	
"	0.065	"	
B	0.063	"	
"	0.065	"	
C	0.063	Not given.	
"	0.065	"	
"	0.065	"	
D	0.0603	"	
E	0.061	Weighs yellow ppt.	
F	0.0666	Magnesia method.	
"	0.0650	"	
"	0.0651	Weigh yellow ppt. original.	
G	0.0660	"	
H	0.061	Magnesia method.	
"	0.065	Titration of solution from the same NH ₄ MgPO ₄ .	

This steel yielded, by the method I have above described, the following results:—

Weight taken. Grms.	KMnO ₄ . C.c.	Correction. C.c.	Phosphorus. Per cent.
3.1264	16.89	0.05	0.0646
3.1267	16.86	0.05	0.0645

The following determination was made in fifty minutes from the start:—

Weight taken. Grms.	KMnO ₄ . C.c.	Correction. C.c.	Phosphorus. Per cent.
3.5014	18.52	0.05	0.0633

Value of 1 c.c. KMnO₄, 0.00012 grm. phosphorus.

A sample of Swedish pig-iron was tried in like manner. The former determinations were:—

No. 5009.			
Method.	Phosphorus. Per cent.		
Emmerton	0.023		
"	0.023		
"	0.023		
"	0.023		
Magnesia Gravimetric	0.023		
"	0.022		

This gave the following by my method:—

Weight. Grms.	KMnO ₄ . C.c.	Correction. C.c.	Phosphorus. Per cent.
3.5187	6.87	0.05	0.0232

* Transactions of the American Institute of Mining Engineers Washington Meeting, February, 1890.

A second determination completed in fifty minutes, P = 0.024.

The method was also applied to iron ore. This was dissolved in hydrochloric acid (1.12 sp. gr.) and filtered. The filtrate was evaporated with nitric acid in the usual way. The residue was fused with excess of sodium carbonate, and then dissolved in the original beaker in dilute sulphuric acid and water. This solution was added to the nitric acid solution, which was transferred to a flask, oxidised with potassium permanganate, and then treated like the iron solution.

No. 4995.—Rubio Ore.

Former Determination.	Phosphorus. Per cent.
Emmertton Method, residue not fused	0.012
fused	0.011
I. "By method" described above	0.013
II. In way described for results, Nos. 4260— 6r, this ore gave	0.0118

Another Bessemer ore, of which the former determinations were as follows:—

No. 5008.

	Phosphorus. Per cent.
Emmertton Method, not fused	0.016
"	0.016
"	0.016
Gave the results by the methods referred to in No. 4995, I. and II.—	
I. Method	0.017
II. "	0.018

There is no loss of time in fusing the residue by this plan, and it is a desirable precaution under any circumstance.

In pig-iron or steel arsenic and titanium interfere with the accuracy of the rapid method. The former must always be separated, and retards the process materially. In fact, the presence of arsenic may be regarded as an obstacle to the determination of phosphorus by any method.

Titanium, probably as titanomolybdate, has an apparent influence on the determination of phosphorus by the rapid method. When the Emmertton method of evaporating the original solution to hard dryness is used, this influence is lessened, but if titanium be present in any appreciable amount the results are vitiated. The following case by each method is a good example:—

No. 4706.—Pig-Iron (containing Titanium).

	Phosphorus. Per cent.
By Mr. Shimer, Mb-Mg method	0.659
By the Emmertton method, modified as in 3680— 81-82	0.649
By the Emmertton method,	0.643
By the "	0.654
By the "	0.650
By the "	0.647
By Rapid Method	0.726
By "	0.719

It may not be amiss to refer to the importance of using a freshly prepared solution of the molybdic acid, which should stand twenty-four hours at least before use. Dr. Drown's formula (*Trans.*, xviii.), has given the best result after several years' trial. The solution must be filtered through asbestos as required.

A summary of the procedure may be found convenient:—

Rapid Method for Pig-Iron or Steel.

- I. Dissolve in 60 c.c. nitric acid (sp. gr. 1.135).
- II. Boil one minute (after action ceases).
- III. Add 5 c.c. potassium permanganate (or until MnO₂ precipitates).

IV. Dissolve the MnO₂ with ferrous sulphate (a few grains usually).

V. Filter into flask (500 c.c. capacity).

VI. Add 10 c.c. NH₄OH (sp. gr. 0.90), or nearly neutralise.

VII. Test for oxidation (III. and IV.) This is done while solution is heating.

VIII. Add 75 c.c. molybdate solution at 85° C., and shake vigorously for five minutes.

IX. Filter and wash with ammoniac sulphate.

X. Dissolve in NH₄OH (sp. gr. 0.96). Observe precautions.

XI. Add 30 to 50 c.c. sulphuric acid (1:2 water) and filter through reductor, observing precautions mentioned (*Trans.*, xvii., 414.)

X. Titrate.

Rapid Method for Iron Ores.

I. Dissolve in hydrochloric acid (1:12 sp. gr.)

II. Filter. Evaporate filtrate with nitric acid (1:20 sp. gr.).

III. Fuse residue with excess of sodium carbonate, and dissolve in dilute sulphuric acid (1:2 water). Combine solutions when the filtrate with nitric acid is ready. Then proceed as above from III. to end.

An accurate determination of phosphorus in pig-iron or steel, in cases uncomplicated by arsenic or titanium, can thus be made in less than an hour. For iron ore but little more time will be necessary.

The three vital conditions of the volumetric method, solution, oxidation, and reduction, by visible reactions, give the method great advantages over any other. From the number of trials made with it the conclusion seems unavoidable that, compared with the "magnesia" method, the results are quite as accurate and certainly more closely accordant. The principles are correct, and I believe that the method can be demonstrated to possess all the requisites for filling the difficult rôle of a standard method.

I wish to acknowledge my indebtedness to Dr. Drown, Mr. A. L. Colby, and Mr. Porter Shimer for samples and valuable information.

ON THE

VARIATION OF THE DENSITY WITH THE CONCENTRATION OF WEAK AQUEOUS SOLUTIONS OF CERTAIN SALTS.*

By Prof. J. G. MacGREGOR, D.Sc.

(Concluded from p. 224.)

Iron Sulphate.—FeSO₄.

Observer:—The author.

Temperature:—20° C.

Formula:— $D_{20} = 0.99827 + 0.0099486 f$.

Percentage of anhydrous salt in solution.	Observed density at 20° C. Grms. per c.c.	Calculated density at 20° C. Grms. per c.c.	Difference.
0.8461	1.00666	1.00669	+0.00003
1.3618	1.01183	1.01182	-0.00001
2.4060	1.02229	1.02221	-0.00008
2.6064	1.02420	1.02420	0.00000

For solutions of iron sulphate, therefore, the above formula holds up to and beyond a concentration of 2.6 per cent.

Copper Sulphate.—CuSO₄.

Observer:—Gerlach.†

Temperature:—18° C.

Formula:— $D_{18} = 0.99866 + 0.0098427 f$.

* From the *Trans. Roy. Soc. Canada*.
† *Fres., Zeit. f. Analyt. Chem.*, viii. (1869), p. 279; *Landolt u. Börnstein's "Phys. Chem. Tabellen,"* p. 147.

Percentage of anhydrous salt in solution.	Observed density at 18° C. Grms. per c.c.	Calculated density at 18° C. Grms. per c.c.	Difference.
0.6390	1.00495	1.00495	0.00000
1.2781	1.01124	1.01124	0.00000
1.9171	1.01764	1.01753	+0.00011
2.5561	1.02403	1.02382	+0.00021
3.1952	1.03052	1.03011	+0.00041

Thus, according to Gerlach, the limit of concentration within which the above formula applies is somewhat less than 2 per cent.

Cadmium Sulphate.— CdSO_4 .

Observer:—Grottrian.*

Temperature:—18° C.

Formula:— $D_{18} = 0.99866 + 0.0097329 p$.

Percentage of anhydrous salt in solution.	Observed density at 18° C. Grms. per c.c.	Calculated density at 18° C. Grms. per c.c.	Difference.
0.282	1.0015	1.00141	-0.00009
1.011	1.0085	1.00850	0.00000
5.08	1.0495	1.04810	-0.00140

These experiments are hardly sufficient for our purpose. Nevertheless they seem to show that in the case of this salt the formula holds up to a concentration of about 3 per cent.

Aluminium Sulphate.— $\text{Al}_2(\text{SO}_4)_3$.

Observer:—Hassenfratz.†

Temperature:—12.5° C.

Formula:— $D_{12.5} = 0.99949 + 0.0092083 p$.

Percentage of anhydrous salt in solution.	Observed density at 12.5° C. Grms. per c.c.	Calculated density at 12.5° C. Grms. per c.c.	Difference.
0.5137	1.00418	1.00422	+0.00004
1.0274	1.00888	1.00895	+0.00007
1.5410	1.01368	1.01368	0.00000
2.0547	1.01838	1.01841	+0.00003
2.5684	1.02307	1.02314	+0.00007

These results show the formula to hold up to a concentration of 2.5 per cent. According to Reuss,‡ as reported in the *Beiblätter zu den Annalen der Physik und Chemie*, Bd. ix. (1885), p. 309, the density of aluminium sulphate solutions for concentrations ranging from 1 to 25 per cent of salt (whether anhydrous or crystallised is not stated) in solution, may be represented by the formula—

$$D_{15} = 1.007 + 0.01 p.$$

Now we know that for $p=0$, $D_{15} = 0.99915$. Hence either this formula is inadequate or the law of the variation of density with concentration is very different for solutions containing between 0 and 1 per cent of salt from what it is for solutions containing between 1 and 25 per cent. Possibly the curve showing the relation between density and concentration is so slightly curved that the densities of solutions within the given limits of concentration may be expressed by the above formula to three places of decimals.

Potash Alum.— $\text{AlK}(\text{SO}_4)_2$.

Observer:—The author.

Temperature:—20° C.

Formula:— $D_{20} = 0.99827 + 0.0095187 p$.

Percentage of anhydrous salt in solution.	Observed density at 20° C. Grms. per c.c.	Calculated density at 20° C. Grms. per c.c.	Difference.
0.7215	1.00512	1.00514	+0.00002
0.7438	1.00535	1.00535	0.00000
1.7260	1.01465	1.01470	+0.00005

According to these experiments the above formula holds up to a concentration of at least 1.7 per cent.

The following observations were made by Gerlach* on solutions of this salt at 17.5° C. The calculated densities are obtained from the formula—

$$D_{17.5} = 0.99875 + 0.009397 p.$$

Percentage of anhydrous salt in solution.	Observed density at 17.5° C. Grms. per c.c.	Calculated density at 17.5° C. Grms. per c.c.	Difference.
2.1792	1.01923	1.01923	0.00000
4.3584	1.04020	1.03971	-0.00049

The comparatively small difference between the observed and calculated density for a solution containing 4.36 per cent of anhydrous salt, makes it probable that the simple proportionality of excess of density of solution over density of water to concentration holds up to a concentration of about 2.5 per cent.

Potassium Sulphate.— K_2SO_4 .

Observer:—Hassenfratz.†

Temperature:—12.5° C.

Formula:— $D_{12.5} = 0.99949 + 0.008595 p$.

Percentage of anhydrous salt in solution.	Observed den. at 12.5° C. Grms. per c.c.	Calculated den. at 12.5° C. Grms. per c.c.	Difference.
1	1.00808	1.00808	0.00000
2	1.01658	1.01658	0.00000
3	1.02517	1.02527	+0.00010
4	1.03377	1.03387	+0.00010

The following is another series of observations of solutions of the same salt:—

Observer:—Gerlach.‡

Temperature:—15° C.

Formula:— $D_{15} = 0.99915 + 0.00816 p$.

Percentage of anhydrous salt in solution.	Observed density at 15° C. Grms. per c.c.	Calculated density at 15° C. Grms. per c.c.	Difference.
1	1.00735	1.00731	-0.00004
3	1.02363	1.02363	0.00000
5	1.04022	1.03995	-0.00027

The above sets of observations agree in showing that the excess of the density of solutions of this salt over that of water at the same temperature is, for solutions which do not contain more than about 2.5 per cent of anhydrous salt, directly proportional to the percentage of anhydrous salt which they contain.

Sodium Sulphate.— Na_2SO_4 .

Observer:—Gerlach.§

Temperature:—15° C.

Formula:— $D_{15} = 0.99915 + 0.0091267 p$.

Percentage of anhydrous salt in solution.	Observed density at 15° C. Grms. per c.c.	Calculated density at 15° C. Grms. per c.c.	Difference.
1	1.00824	1.00827	+0.00003
2	1.01734	1.01740	+0.00006
3	1.02653	1.02653	0.00000
4	1.03562	1.03565	+0.00003
5	1.04491	1.04478	-0.00013
6	1.05410	1.05391	-0.00019

These experiments would seem to show that the above formula holds in the case of sodium sulphate for solutions containing from 0 to 4 per cent of anhydrous salt. The following are other observations with the same salt:—

* *Beiblätter ann. phys. Chem.*, xi. (1887), p. 217.

† *Ann. de Chim.*, xxviii. (1759), p. 296.

‡ Gerlach's "Specifische Gewichte der gebräuchlichsten Salzlösungen," Freiberg, 1859; and "Jahresbericht u. Fortschritte d. Chem.," 1859.

§ Fresenius, *Zeit. f. analyt. Chem.*, viii. (1869), p. 279; and Landolt u. Börnstein's "Phys.-chem. Tabellen" (1883).

* *Weid. Ann.*, xviii. (1883), p. 191.

† *Ann. de Chim.*, xxviii. (1799), p. 296.

‡ *Chem. Ber.*, xvii. (1884), p. 2888.

Observer:—Ostwald.*

Temperature:—15° C.

Formula:— $D_{15} = 0.99915 + 0.0091875 p$.

Percentage of anhydrous salt in solution.	Observed density at 15° C. Grms. per c.c.	Calculated density at 15° C. Grms. per c.c.	Difference.
2	1.0176	1.01753	-0.00007
4	1.0359	1.03590	0.00000

Thus Ostwald's experiments give the same result.

Caustic Potash.—KHO.

Observer:—Thomsen.†

Temperature:—18° C.

Formula:— $D_{18} = 0.99866 + 0.0093717 p$.

Percentage of anhydrous salt in solution.	Observed density at 18° C. Grms. per c.c.	Calculated density at 18° C. Grms. per c.c.	Difference.
1.5344	1.01304	1.01304	0.00000
3.0224	1.02702	1.02698	-0.00004
5.8674	1.05359	1.05364	+0.00005

The following are other observations with the same substance:—

Observer:—Kohlrausch.‡

Temperature:—15° C.

Formula:— $D_{15} = 0.99915 + 0.0092959 p$.

Percentage of anhydrous salt in solution.	Observed density at 15° C. Grms. per c.c.	Calculated density at 15° C. Grms. per c.c.	Difference.
4.19	1.0381	1.0381	0.0000
8.42	1.0778	1.0774	-0.0004

Thomsen's experiments show that in the case of solutions of caustic potash, even up to a strength of more than 5 per cent, excess of density over that of water is practically proportional to the percentage of salt. Kohlrausch's results substantiate Thomsen's; for, as is seen above, a formula in which k is chosen so that the density given by it is exact for $p = 4.19$, gives a density for $p = 8.42$, which is not very far wrong.

Caustic Soda.—NaHO.

Observer:—Thomsen.§

Temperature:—18° C.

Formula:— $D_{18} = 0.99866 + 0.014563 p$.

Percentage of anhydrous salt in solution.	Observed density at 18° C. Grms. per c.c.	Calculated density at 18° C. Grms. per c.c.	Difference.
0.8528	1.01105	1.01108	+0.00003
1.6871	1.02323	1.02323	0.00000
3.3023	1.04719	1.04675	-0.00044

The formula therefore holds for solutions of strengths ranging up to about 2 per cent, but not for solutions of greater strength. Caustic soda thus differs in a marked manner from caustic potash.

The above are the only salts for which I have been able to obtain, or to find, data to determine the limits of concentration within which formulæ of the above kind hold—within which, in other words, the concentration-density curves of their solutions are, to the fourth place of decimals, straight lines. In the case of most salts, the weakest solutions, whose densities have been examined, are already beyond the limits referred to.

The table given below contains a list of the values of k found above for the various salts examined.

It will be noticed that in most cases the values of k do not differ from one another to any considerable extent. Now, k is the rate of increase of the density with the strength of a solution when its strength is but small; hence, the densities of dilute solutions of these salts increase with their strength at rates which do not differ

greatly in the case of the different salts; or, in other words, the concentration-density curves of sufficiently dilute solutions of these salts are not only practically straight lines, but are nearly equally inclined to the axis of concentrations.

Substance.	Temperature.	k .	Observer.
ZnSO ₄	20.0° C.	0.0103918	The author.
MgSO ₄	20.0	0.0106324	"
"	23.0	0.0098176	Schiff.
FeSO ₄ ..	20.0	0.0099486	The author.
CdSO ₄	18.0	0.0097329	Grotian.
CuSO ₄	18.0	0.0098427	Gerlach.
Al ₂ (SO ₄) ₃	12.5	0.0092083	Hassenfratz.
AlK(SO ₄) ₂	20.0	0.0095187	The author.
K ₂ SO ₄ ..	15.0	0.0081600	Gerlach.
"	12.5	0.0085950	Hassenfratz.
Na ₂ SO ₄	15.0	0.0091875	Ostwald.
"	15.0	0.0091267	Gerlach.
KHO	18.0	0.0093717	Thomsen.
NaHO..	18.0	0.0145630	"

NOTICES OF BOOKS.

Chemical Arithmetic. Part I. A Collection of Tables, Mathematical, Chemical, and Physical, for the Use of Chemists and Others. By W. DITTMAR, LL.D., F.R.S.E. (London and Edinburgh), Professor of Chemistry in the Glasgow and West of Scotland Technical College. Glasgow: W. Hodge and Co.

WHETHER the title of this work is quite appropriate or not, it differs broadly from two works which have recently come under our notice. Part I., now before us, is, according to the author, a new edition of his "Tables to Facilitate Chemical Calculations," though with changes and additions. He aims at supplying the chemist, scientific and technical, with a "collection of what he needs of mathematical auxiliaries, and of chemical and physical constants," and that without going further.

We scarcely see that any apology is needed for the utilisation of logarithm tables. Such matter has by this time become common property, and he who makes use of it is surely not open to the charge of "piracy." In such tables Dr. Dittmar's work is rich. There are two tables, Nos. 1 and 2, of three-place logarithms, a table of four-place and one of five-place logarithms.

Then follow a table of formula-values of a number of substances and radicles, and their logarithms.

The table headed "Analytical Factors and their Logarithms" is for the purpose of calculating from the weight of a substance found, as the result of some analytical process, the weight of some constituent required, e.g., found, barium sulphate; required, sulphuric acid. We do not see that the table here given is as convenient as that found in Rose's "Quantitative Analysis."

There are, in addition, certain empirical factors, e.g., in connection with the chloroplatinate method for determining potassium and ammonium; and for the determination of sugars by means of Fehling's solution.

We have also tables for gas, volumetric determinations for nitrogen, carbonic acid, nitric acid, and oxygen.

In the comparison between the metric and the British systems of weights and measures, the author proposes the fluid gramme as a more convenient unit for the measurement of liquids than the c.c. or the litre. This unit designates the volume at 15° C. of a quantity of water, the uncorrected weight of which, determined in air at 15° C. and 760 m.m. pressure by means of brass weights = 1 grm. Prof. de Koninck proposes to use the name "Mohr" for 1000 fluid grms., and "millimohr" for the fluid grm. itself. The author remarks that "what in commercial volumetric apparatus figures as c.c. litre comes, as a rule, nearer to our fluid grm. and litre respectively, than to the ostensible units."

* *Journ. f. prakt. Chemie*, xxii. (1880), p. 305.

† "Thermo-chemische Untersuchungen," Bd. i., p. 47.

‡ *Weid. Ann.*, vi. (1879), p. 21.

§ "Thermo-chemische Untersuchungen," Bd. i., p. 47.

We cannot help remarking that the British system loses much of its apparent complexity if, as units, we confine ourselves to the grain and the grain measure, with their multiples and sub-multiples, rigorously eliminating cubic inches, drachms, scruples, ounces, and minims.

In the table of Hydrometer Scales, the author gives only two of the varieties of Baumé's scale, not to speak of the arbitrary fluctuations which it experiences in the hands of careless glass-blowers.

Further sections of the work are taken up with the relations between specific gravity and percentage of solution in a number of solutions; corrections of weighings; the reduction of the specific gravities for solids and liquids; calibration of volumetric apparatus; gas-analysis; gas-absorption; and thermometry.

To all persons concerned with the study of general chemistry, or of chemical physics, this work cannot be too strongly recommended.

Book A; or, Arithmetical Chemistry. Part I. By C. J. WOODWARD, B.Sc. London: Simpkin, Marshall, and Co. Birmingham: Cornish Bros.

THIS little book, in many respects, reminds us of its companion volume "*Book D; or, Arithmetical Physics*," which it became our duty to notice a few weeks ago. The "General Preface" in both is admittedly the same, and is substantially a "defence of examination questions"; consequently, our remarks on that treatise must apply to the one before us.

In the "Introduction," however, we find a passage which must command approval. Says Mr. Woodward:—"Then came a period in which, at any rate to those who were guided by the requirements at South Kensington, a complete and unfortunate reversal took place. This was the age of graphic formulæ, when, owing to the necessity of turning out an article to bring the highest price to the producer, both teachers and students, intent on fitting "bonds" in order to satisfy the examiners, were apt to ignore the experimental evidence upon which the laws of chemical combination rest."

This quotation shows how little examiners are to be trusted. It is not too much to say that at the time referred to by the author a student, even if he were a rival of Mendeleeff in the philosophy of chemistry, if his analytical skill were equal to that of Fresenius, or his success in effecting novel and interesting syntheses on a level with that of Baeyer, still, lacking the power of playing at the game of bonds, would have been ignominiously rejected. That such could be the case is, of course, a fresh count in the indictment of the examination system to which officialism clings so devotedly, whilst the nation looks on in apathy.

Much of the matter here to be found is, in substance, what was formerly taught as stoichiometry.

Inorganic Chemistry: the Chemistry of the Non-Metals. By J. OAKLEY BEUTTLER, M.A. London: Relfe Brothers.

HERE is an addition to the numerous array of elementary works on chemistry. The author restricts himself to a consideration of the non-metals, possibly intending to treat of the metals in a future volume.

The object of the book is strictly examinational. We are, indeed, told in the preface that "these notes have been compiled to cover the ground required by the London Matriculation Examination, the Cambridge Local Examining Board, and the Science and Art Department." But, we cannot help asking, are there not manuals already in existence which cover this ground, and, if so, *cui bono*?

In the first chapter, the author defines an element as "that substance which cannot be split up any further." It would surely be safer to say which hitherto has not been split up any further. Mr. Beuttler apparently

recognises only sixty-four elements, and gives the atomic weights not, in all cases, according to the most recent and accurate determinations. Thus, the atomic weight of gold is here still stated to be lower than that of platinum.

In the occurrence of the non-metals in nature, the reader is told that sulphur occurs in volcanic districts, and "combined with various ores." Would it not have been better to say "combined with metals forming various ores"? The presence of carbon in the form of carbonic acid in many minerals, and that of phosphorus in apatite, vivianite, &c., is omitted.

The account given (on p. 26) of the reaction produced on dropping a piece of sodium into water is scarcely satisfactory, as we find no mention of the oxygen liberated from the water.

On pp. 32 and 33 we find the account of the uses of chlorine given twice.

Graphite, we read, is obtained from mines of Cumberland. Far larger quantities are now raised in Ceylon and Siberia.

It is in these days incorrect to say that fuming sulphuric acid is "principally manufactured at Nordhausen, in Saxony."

The preparation of free fluorine and its properties have been omitted.

The notice of Marsh's arsenic test is obscure. Mr. Beuttler writes:—"Add pure zinc and sulphuric acid, light the arseniuretted hydrogen, and a grey ring will be deposited or a cold piece of porcelain inserted in the flame." This passage can only be understood by reading *on* instead of *or*.

Five hundred grms. of potassium nitrate (p. 118) are to be strongly heated until it is entirely converted into "potassium nitrate." The chemist will at once see that here potassium *nitrite* must be meant in the second place; but will the "ordinary pupil" see his way out of the difficulty?

This book would be much improved by revision, in which some needless repetitions should be cancelled, and various typographical errors eliminated. If more examination manuals are needed, they should, at least, be correct.

CORRESPONDENCE.

THE ALCOHOL TEST FOR CASTOR OIL.

To the Editor of the Chemical News.

SIR,—The criticisms and observations by Mr. J. Arthur Wilson in CHEM. NEWS, vol. lxii., p. 215, have all been anticipated. In every reprint of the British Pharmacopœia issued in and since 1886, castor oil has been stated, correctly, to be soluble in *four* times its volume of spirit of wine—of course, of the official strength and at the official temperature.

Draper, Cripps, Allen, and Conroy have all preceded Wilson in drawing attention to the fact that the extent of the solubility depends either on the amount, the strength, or the temperature of the spirit.—I am, &c.,

THE ANNUAL REPORTER ON THE PHARMACOPŒIA
TO THE MEDICAL COUNCIL.

17, Bloomsbury Square, London,
November 3, 1890.

Assaying.—Mr. W. Heinemann will issue in a few days a new edition of Brown's "*Manual of Assaying Gold, Silver, Copper, and Lead Ores*." The work has been revised, corrected, and considerably enlarged; and a chapter on the Assaying of Fuels, by Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c., has been added. The book contains 333 pages, crown 8vo., and is illustrated with 89 figures.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 15, October 13, 1890.

Combinations of Mercury Cyanide with the Salts of Lithium.—Raoul Varet.—The compounds here described are mercury lithium iodocyanide, and the corresponding bromine and chlorine salts.

Researches on the most Suitable Conditions for the Preparation of Mono-isobutylamine on the Large Scale.—M. Malbot.—The author has shown that the different terms of the amines are not produced simultaneously, according to the equations of Hofmann, but successively by a series of transformations, the totality of which forms the progression of the amines.

On a General Procedure for the Synthesis of the Nitriles and the β -Ketonic Ethers.—L. Bourcault.—This memoir is not adapted for abstraction.

On the Presence and the Disappearance of Trehalose in Mushrooms.—E. Bourquelot.—The author's experiments show that the disappearance of trehalose is really connected with the vegetation of the mushroom, and takes place much more rapidly than it has been supposed. They explain why the chemists who have analysed *Lactarius piperatus* have merely found mannite.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., April, 1890.

Explosives without Smoke.—Sir F. Abel.—A discourse delivered before the Royal Institution.

On the Sensitiveness of certain Explosives to Percussion.—A. Werner Cronqueit.—From *Chemical Industry*.

Novel Applications of the Oleorefractometer.—E. H. Amagat and F. Jean.—According to the investigations made on behalf of the "Société des Agriculteurs" of France, this instrument may be successfully applied to the detection of sophisticated butters, oils, &c.

New Method of Analysis Applicable to Industrial Waters which have to undergo a Chemical Purification, and to Feed-waters for Steam Boilers.—Leo Vignon.—In order to determine the elements of chemical purification, or the anti-incrustation agents, it is sufficient to determine the free or the half-combined carbonic acid, and to determine the quantity of sodium carbonate necessary to convert the soluble salts of calcium and magnesium into carbonates which are chemically neutral.

Determination of Potassa and Humus in Soils.—J. Raulin.—(Already inserted; CHEM. NEWS, vol. lxi., p. 154).

Industrial Production of Aluminium Alloys by Electric Action.—H. J. Dagger.—From the *CHEMICAL NEWS*.

The Colourations of Tempered Steel.—Thomas Turner.—From *Proceedings of Birmingham Philosophical Society*.

Magnesium Bronze.—H. N. Warren.—From the *CHEMICAL NEWS*.

Contribution to the Study of Mineral Oils for Lubrication.—Aug. Lunkler (*Dingler's Polyt. Journal*).—This long essay does not admit of useful abstraction.

Ozokerite.—Platz (*Zeit. Angew. Chemie*).—The author condemns the method of extracting ozokerite.

Researches on Narcotine.—W. Roser.—From *Liebig's Annalen*.

Purification of Coal-gas by Means of Oxygen.—W. A. Valon (*Chemiker Zeitung*).—An account of the process as tried at Ramsgate.

Constitution of Antipyrine.—G. Patein.—This compound is now considered not as dimethyloxyquinizine, but as phenyldimethylpyrazole.

New Method of Determining Uric Acid in Urine.—Dr. Bayrac.—This memoir requires the accompanying illustration.

On the Analysis of Slates.—F. Reverdin and Ch. de la Harpe.—The destruction of slates is due to three causes: two of them chemical in their nature, and one—the most important—physical. These are:—The chemical action of atmospheric agents, — the least important; (2) the chemical action of gases emanating from the woodwork of the roof; (3) the physical action due to unequal thermic conduction. The chemical action is exerted on surfaces only, and renders the material pulverulent. The physical action extends to the entire mass and multiplies the surfaces capable of being attacked by chemical influences.—*Chemiker Zeitung*.

Conditions in which Portland Cement cannot Set.—Schiffner (*Chemiker Zeitung*).—Cement mortar kept covered and moist for twenty-seven days hardened perfectly. If, after being mixed, it is preserved from moisture it remains soft and friable.

On the Ramie Fibre.—J. Arnaudon.—If ramie is prepared with tannin and red liquor it dyes up much better with oranges, ponceaux, and bordeaux, and the colour is not removed by washing.

Silks Dyed and Weighted (*Romew's Journal*).—For practising this fraud upon coloured silks, there is used an extract of gall-nuts or of sumac, and the silk is then dyed with aniline colours. Pure whites, and light shades, cannot be obtained in this manner.

A New Process of Bleaching.—Dr. Kassner (*Romew's Journal*).—As an oxidising agent, the inventor proposes a mixture of potassa and potassium ferricyanide. The ferrocyanide formed is re-oxidised to ferricyanide as follows:—A solution of sodium carbonate is heated with calcium plumbite; the precipitate and lead bi-oxide is suspended in the exhausted ferrocyanide, heated, and a current of carbon dioxide from a coke furnace is passed into the liquid. Ferricyanide is re-formed, and a mixture of lead and calcium carbonate is deposited.

Journal für Praktische Chemie.
New Series, Vol. xli., Part 8.

Contributions to a Knowledge of the Analogies existing between Keton Acids and Sulphone-carbon Acids.—Adalbert Rössling.—The principal results of these results are:—1. The β sulphone-carbon acids do not undergo an acid splitting. 2. The metal atom of the sodium phenyl-sulphonacetate cannot be substituted by acid residues. Substituted esters containing an acetyl and a sulphone group on the same carbon atom cannot be obtained by the action of sodium benzoisulphonate upon mono- and dichloroacetic esters. 3. The action of iodine upon sodium phenylsulphone acetate in presence of water in alcoholic solution gives rise, not to a diphenylsulphonised succinic ester, but only to iodomethylphenylsulphone. The formation of mono- and diphenylsulphonised succinic acid cannot be effected by the action of a benzenesulphonate upon mono- and di-bromosuccinic acid. Chloroxalic ester acts upon sodium benzenesulphonate almost exclusively, with the formation of carbonic acid, benzenedisulphoxide, and oxalic diethylester; there is also formed a small quantity of phenyl-sulphonketonic ester. Nitrous acid produces from phenylsulphonacetate a compound $(C_6H_5SO_2)_2NHO$, with a simultaneous splitting off of carbonic acid and oxidation of the methylene group. Concentrated nitric acid produces

from phenyl-sulphonacetic acid phenyl-nitroso-sulphon, $C_6H_5SO_2NO$, with abscission of carbon dioxide and oxidation of the methylene group.

Parts 9 and 10.

The Constitution of the Cobalt Bases.—S. M. Jørgensen.—This memoir, though very interesting, does not admit of abstraction.

On Meta-Diamine Compounds.—S. M. Jørgensen.—We find here an account of ethylene diamine-dichloropraseo cobalt platinous chloride, ethylene diamine dichloropraseo cobalt bromide, the corresponding dibromo-praseo cobalt bromide, ethylene diamine dibromo-praseo cobalt bromide hydrogen bromide, ethylene diamine dibromo-praseo cobalt nitrate, ethylene diamine dibromo-praseo cobalt-platinum chloride, ethylene diamine dibromo-praseo cobalt mercuric chloride, ethylene diamine dichloro-violeo cobalt chloride, and a number of other analogous compounds of the purpureo-cobalt bases.

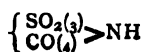
On the α -dichlor Substitute of Symmetrical Dimethylsuccinic Acid.—R. Otto and G. Hest.—The results of the experiments detailed are:—It is not possible to convert the α -dichlor acid dimethylsuccinic acid into a geometrically isomeric compound by means of its anhydride. The anhydride of the α -dichlor acid dimethylsuccinic acid can be converted into the ammonium salt of the α -dichlor acid dimethyl succinamic acid by alcoholic ammonia. On heating an aqueous solution (a) of the alkali salt, or on heating the free acid with water in a tube to 120° (b), there are produced α -methyl- β -chlorcrotonic acid and methylethylketone. If heated with strong hydrochloric acid to 140° - 150° in a tube α -methyl- β -chlorcrotonic acid yields no addition product of HCl, but at once splits off CO_2 , a dichlorotulian being probably formed.

Researches from the Laboratory of the University of Freiburg.—These comprise the following memoirs:—On the mixed fatty-aromatic ketones and their oxidation by permanganate, by Ad. Claus. On acetone chloroform, chlor-isobutyric trichloride, and acetone-chloroform ether, by C. Willgerodt and Schiff. On the stereo-chemistry of the compounds of the elements of the nitrogen group, by C. Willgerodt.

Revue Générale des Sciences Pures et Appliquées.
Vol. i., No. 18, September 30, 1890.

Lavoisier according to M. Berthelot.—L. Olivier.—This paper is in some sort a reply to the discourse of Professor Thorpe, delivered at the late meeting of the British Association. M. Olivier asserts that Professor Thorpe has merely revived "the ancient quarrel between sagacious inventors (he means discoverers) of particular facts and the men of genius who discover general theories." [We must be permitted to say that Professor Thorpe, as a careful and conscientious perusal of his address will show, has neither done nor attempted such a task. His great object has been to rebut the claim set up on behalf of Lavoisier as the first, or at least as an independent, discoverer of oxygen, and the assertion that the composition of water had been "prepared by Cavendish and realised by Lavoisier," and in this rebutter he is perfectly successful]. M. Olivier disclaims, on behalf of Lavoisier, the priority in the use of the balance and the authorship of the saying that "nothing is lost and nothing created."

Methyl Saccharine, a new Sugary Matter.—Kronberg.—This compound is a higher homologue of the "saccharine" of Fellberg and Remsen. The group common to the two compounds is—



October 15, 1890.

The Liquefaction of the Alloys of Gold and Platinum.—E. Matthey.—Translated from the *Proceedings of the Royal Society*.

MISCELLANEOUS.

The Reorganisation of the Royal School of Mines.—Our readers will doubtless have learned from the morning papers that, by the Queen's command, the "Normal School of Science" and the "Royal School of Mines" will in future be known as the "Royal College of Science." We, however, wish it to be clearly understood that for the future, as in the past, those who pass in mining and metallurgy will receive the Associateship of the "Royal School of Mines." The distinctive character of the Associateship will thus be unequivocally retained.

The New Professor of Chemistry at the University of Aberdeen.—A meeting of the Aberdeen University Court was held on October 29th to appoint a Professor of Chemistry, *vice* the late Professor Carnelley. Dr. Francis R. Japp, Ph.D., F.R.S., Assistant Professor of Chemistry at the Royal College of Science, South Kensington, was unanimously elected. The new Professor, who is forty-two years of age, is a Master of Arts, and Honorary Doctor of Laws of the University of St. Andrews, and a Doctor of Philosophy of the University of Heidelberg, where he studied inorganic chemistry for three years under Professor Bunsen. He subsequently studied organic chemistry for a year and a half under Professor Kekulé, of Bonn, and worked in the laboratory of Professor Crum Brown, in Edinburgh. Twelve years ago he became a member of the teaching staff of the South Kensington Science Schools, where, in 1881, he was appointed to the newly-created assistant professorship of chemistry. He is the foreign secretary of the Chemical Society, and has served on the Council of the Institute of Chemistry of Great Britain and Ireland. He has contributed a number of memoirs to the Journal of the Chemical Society, and is the author of several articles in the revised editions of "Watts' Dictionary of Chemistry." We may mention that Dr. Japp was a candidate for the chair when Professor Carnelley was appointed.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Gelatinising Petroleum.—Can any reader inform me which is the best way of making a petroleum jelly by boiling it with soap? Does the quality of the petroleum affect the result, and what quantity of soap should be used? The jelly should be as soft as possible, and of as low a specific gravity as possible.—D. U.

MEETINGS FOR THE WEEK.

FRIDAY, 14th.—Physical. "On Certain Relations Existing among the Refractive Indices of some of the Chemical Elements," by the Rev. T. Pelham Dale, M.A. "Tables of Spherical Harmonics" (with examples), by Prof. Perry, F.R.S.

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3rd November, 1890.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1616.

ON THE PHOSPHORESCENCE OF LITHIUM COMPOUNDS IN VACUO, AND THE SPECTRA OF COATED TERMINALS.

By E. E. BROOKS.

HAVING noticed the great brilliancy with which certain lithium compounds phosphoresce, when examined by Mr. Crookes's method in the negative discharge *in vacuo*, it may perhaps be of some interest to state the results obtained.

Lithium sulphate gave a bright lilac-blue glow.

Lithium phosphate was equally brilliant, the colour being a light Cambridge blue.

Lithium Chloride.—Pale lavender-blue, only moderate brilliancy.

Lithium Fluoride.—Very light flesh-coloured glow, about equal to the chloride in brilliancy.

Lithium Silico-fluoride.—Deep blue, with darker spots, but not so brilliant as the somewhat similar phosphorescence of the sulphate.

Lithium phosphate fused with sodium carbonate, gave a bright emerald-green glow, which existed unchanged for a second or two after circuit was broken, and then faded quickly away. The other salts above mentioned appeared to have no residual glow.

The nitrate, carbonate, and hydrate did not show any signs of phosphorescence.

Some lithium nitrate was fused and partly volatilised *in vacuo*, and the glass in contact with the fused salt received an opaque enamel-like coating, apparently unaffected by water or acids; and, when the tube was again exhausted, this white coating exhibited a distinct phosphorescence, similar to, but more yellowish than, the normal phosphorescence of the German glass tube.

Of the lithium minerals, I believe spodumene is the only one mentioned by Mr. Crookes. This gives a golden yellow glow.

Lepidolite phosphoresces with very great brilliancy. The colour is a deep red, with traces of blue.

Petalite is also exceptionally brilliant, glowing with a rich yellow, like a live coal.

The spectra of all the above salts and minerals are continuous, only showing a concentration of light in certain parts of the spectrum.

Rubellite and indicolite did not phosphoresce, and amblygonite gave only slight traces of a whitish glow.

While working with lithium salts, certain peculiarities were noticed, which led to extended experiment, but, at present it is only intended to give a brief preliminary notice of the results obtained. It was found that when a plate of aluminium or platinum was coated with a thin layer of a lithium salt, either by fusion or merely lying loosely upon it, and then made the negative terminal *in vacuo*, it glowed with a conspicuous red light, the spectrum of which consists of two lines, red and orange, of which the orange line is slightly the most brilliant.

By direct comparison, the red line was found to coincide with the flame line of lithium; and, although a similar test has not yet been applied to the orange line, which is not visible in the flame spectrum, it is most probably the well known β -line of lithium.

A similar effect was obtained in other cases.

A terminal coated with thallium sulphate gave a green line which coincided with the green thallium flame line.

A sodium coating gave a very strong D line, the yellow glow extending some distance from the terminal.

A calcium nitrate coating gave the orange and green bands of the metal, which were directly compared with the flame spectrum.

A barium nitrate coating gave several green lines, and an orange line near D.

These results were obtained with a 1-inch spark coil. Other metals gave only faint spectra, or none at all; but with a stronger discharge the method might be more successful.

It is important to note that these spectra almost wholly disappear in a high vacuum, and are only well seen through a comparatively small range of pressure. The best effects are obtained when the dark space extends about $\frac{1}{4}$ -inch from the terminal, and as at this pressure the lines due to the gas used are still fairly brilliant, the two spectra are seen together.

Countess Street, Leicester.

THE DETERMINATION OF SULPHUR IN COPPER.

By H. JOSHUA PHILLIPS, F.C.S.

ALTHOUGH modern refined copper is, as a rule, very free from sulphur, yet since such small quantities of this element seriously affect the physical properties of the metal, a very accurate method for its determination becomes imperative.

The estimation of sulphur in a nitrate solution, by precipitation with barium chloride or nitrate, gives results below the truth—owing to the solubility of the resulting basic sulphate in the solution of nitrate of copper, and, indeed, appreciable quantities may be overlooked altogether. Good results, however, can be obtained in a chloride solution.

The following is the process used by the writer:—

Ten grms. of the sample is dissolved in pure 16 E nitric acid (= sp. gr. 1.42), and evaporated to dryness on the water-bath, the residue is taken up with 400 c.c. of E nitric acid solution and filtered, if necessary, and any residue reserved. The filtrate is diluted to 800 c.c., and heated to 70° C., 1 c.c. of 5 E HCl is added, and the solution well stirred and allowed to stand in a dark place for twelve hours. The supernatant liquid is now decanted as far as possible from the precipitate of silver chloride, and finally filtered and washed, and the silver determined, if necessary, in the usual manner. The filtrate is now evaporated nearly to dryness, and 50 c.c. of pure 10 E HCl (= sp. gr. 1.16) added, and the evaporation continued to complete dryness. The residue is dissolved in a minimum quantity of water, and another 50 c.c. of 10 E HCl added and again evaporated to complete dryness. The residue is dissolved in 300 c.c. of E HCl and diluted to 700 c.c., heated to boiling, and 2 c.c. of E baric chloride solution added, stirred, and allowed to stand twenty-four hours. The baric sulphate is then filtered off and treated as usual. To test the method, 10 grms. of pure electrotype copper, free from sulphur, was treated as above, and a quantity of copper sulphate added, representing 0.1 per cent of sulphur on the 10 grms., and the result obtained gave 0.098 per cent sulphur. The reserved residue, insoluble in nitric acid, is fused and tested for sulphur; and, if any is present, it is estimated and added to the portion already found in solution.

Usually, the amount of lead present in a copper is over and above the theoretical quantity necessary to form sulphate of lead with the proportion of sulphur present on treatment with nitric acid, and one might expect the sulphur, present as lead sulphate, to be practically all in the insoluble residue, but since PbSO₄ is so soluble in the nitrate of copper solution, it frequently happens, in fairly pure coppers, that the whole goes into solution, and hence

has to be determined by some such method as the foregoing.

G. E. Ry. Laboratory, Stratford, London, E.

THE ACTION OF LIGHT UPON THE DIAZO COMPOUNDS OF PRIMULINE AND DEHYDROTHIOTOLUIDINE.*

(A METHOD OF PHOTOGRAPHIC DYEING AND PRINTING).

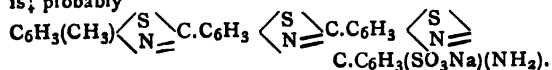
By ARTHUR G. GREEN, CHARLES F. CROSS, AND EDWARD J. BEVAN.

IN the early part of 1887, one of us (Green) discovered that by heating paratoluidine (2 mols.) with sulphur (4 to 5 atoms) at 200°–300° C. a very complex amido base was obtained, which, on treatment with fuming sulphuric acid at a low temperature, was converted into a sulphonic acid, the alkaline salts of which were easily soluble in water, and had the peculiar property of dyeing cotton primrose yellow from an alkaline or neutral bath without the use of a mordant. Further, the amido compound thus fixed upon the fibre could be diazotised *in situ* by passing the material through a weak solution of nitrous acid, and when diazotised could be combined with various phenols and amines, thus producing a variety of different colours, which, being formed within the fibre, were all distinguished by great fastness to washing, &c. The soluble amido sulphonic acid was named "Primuline" by its discoverer, and has found a very extensive employment in cotton dyeing; the colours produced from it within the fibre were called "Ingrain Colours."[†]

Although the chemical constitution of primuline base (of which primuline is the mono-sulphonic acid) has not yet been determined with certainty, there is no doubt that it is a condensed derivative of dehydrothiotoluidine, a body which always accompanies it in its formation, and that it differs from the latter in exactly the same way as dehydrothiotoluidine itself differs from para-toluidine. As there is scarcely any doubt that dehydrothiotoluidine has the formula—



i.e., is an amido-benzoyl-amido-thi-cresol, it follows that the formula of primuline, or rather of its chief constituent is[‡] probably



In a similar manner, by heating meta-xylylidine or pseudo-cumidine with sulphur, homologues of primuline are obtained, which, like primuline itself, dye cotton without a mordant, and can be diazotised and combined with phenols within the fibre.

It has been long observed by one of us (Green) that the diazo compound of primuline was very sensitive to the action of light, being readily decomposed thereby, and losing its property of combining with phenols and amines. Upon this fact we have now founded a photographic process, by means of which designs can be produced in fast colours upon cotton, silk, wool, linen, or other fabrics. It can also be applied to wool, xylonite, celluloid, paper, or to gelatin films upon glass, thus affording a very wide range of employment. The process, which is a very simple one, merely depends upon the fact that if a material containing diazotised primuline be exposed to light under a design, those parts which are acted upon by light will be decomposed, whilst the parts protected from the light will remain unaltered, and consequently, on sub-

sequent development with a phenol or amine, will produce colours, whilst the decomposed portions will not. The details will, of course, depend somewhat upon the material to be treated. As an instance we may take the production of a design upon cotton cloth, cotton velveteen, &c. The material is first dyed with primuline from a hot bath containing common salt until the required depth is obtained. It is then washed and diazotised by being immersed for a quarter of a minute in a cold bath containing about $\frac{1}{2}$ per cent of sodium nitrite, and strongly acidified with sulphuric or hydrochloric acid. The material is washed again and exposed damp (or if preferred after having been dried in the dark), to the action of light beneath leaves, ferns, flowers, or other natural objects, or beneath glass or transparent paper, upon which may be painted or printed any design which it is required to copy. Either the arc electric light or daylight may be employed; in the latter case the time of exposure will of course vary with the intensity of the light; under half a minute is required in bright sunshine, and nearly half-an-hour in very dark cloudy weather. When the decomposition is complete, which may be readily ascertained by means of a test slip, exposed simultaneously, the material is removed from the light and either passed into the developing bath at once, or is kept in the dark until it is convenient to develop it. The developing bath consists of a weak solution ($\frac{1}{2}$ to 1 per cent) of a phenol or amine made suitably alkaline or acid, the phenol or amine employed depending upon the colour in which it is required to produce the design, thus:—

For red, an alkaline solution of beta-naphthol.
" maroon, " beta naphthol-di-sulpho-phenol. [luc acid.
" yellow, " resorcin.
" orange, " phenylene diamine hydrochloride.
" brown, " alpha-naphthylamine hydrochloride.
" purple, "

If it is required to produce the design in two or more colours, the respective developers, suitably thickened with starch, may be applied locally by means of a brush or pad. After development the material is thoroughly washed and requires no further fixing.

Linen, silk, and wool are treated in exactly the same way. Paper for copying drawings, &c., is coated on the surface with primuline by means of a brush or roller. For the production of gelatin films upon glass the primuline is incorporated with the gelatin before being applied to the glass.

In place of ordinary primuline the homologues already mentioned may be used; for silk and wool the primuline may be replaced by dehydrothiotoluidine-sulphonic acid, by means of which colourless backgrounds may be obtained.

Concerning the reaction which occurs when the diazo-primuline or the diazo-dehydrothiotoluidine is decomposed by light, we cannot at present say anything definite, except that the diazo group is completely destroyed, for on treatment with sodium hydrosulphite (true hyposulphite), it cannot be converted into the amido-group (re-forming primuline or dehydrothiotoluidine). The reaction may consist in a replacement of the N_2 group by OH or by H, or may be even more complex. Although we cannot affirm that this reaction to light is a property of the diazo-compound of this group of bodies only, yet it is certain that they possess an extreme susceptibility to light far greater than that of other diazo-compounds, whilst at the same time they are far more stable to heat. It is thus possible that this property may depend in some way upon the sulphur which they contain.—*Chemical Trade Journal*.

Appointment.—Mr. Charles H. Southwell, Pharmaceutical Chemist (Exam.), of Boston, was appointed Public Analyst for the Holland Division of Lincolnshire at a Statutory Meeting of the County Council on November 7th.

* Read before the British Association, Leeds Meeting, 1890.

† A. G. Green, *Journ. Soc. Chem. Ind.*, (1888), p. 179.

‡ A. G. Green, *Journ. Chem. Soc.*, (1889), p. 227; *Ber.*, 22, 968; P. Jacobson, *Ber.*, 22, 330; L. Gattermann, *Ber.*, 22, 422; W. Pfützing and L. Gattermann, *Ber.*, 22, 1063.

DETERMINATION OF METALLIC ALUMINIUM IN THE ALUMINIUM OF COMMERCE.

By G. KLEMP.

THE striking solubility of aluminium in alkaline lyes, presents means—which do not prove available in the determination of zinc powder in consequence of the relatively sparing solubility of zinc—to effect the determination of aluminium in a simple manner. A weighed quantity of the aluminium is treated with potassa-lye, and the escaping hydrogen is determined either volumetrically as gas or gravimetrically as water. For the former purpose most of the apparatus used for gas volumetry may be employed (especially Lunge's improved gas volumeter), and for the latter method the apparatus which R. Fresenius proposes for his method of determining zinc powder.

Fr. Schulze made use of the gas-volumetric method in order to compare the quantities of hydrogen gas evolved by different sorts of aluminium in alkaline solutions, which he designated as approximately corresponding to the proportion of pure aluminium. But, according to the instances given, it is not possible to arrive at a decisive conclusion, either as to the quantity of the aluminium present or the applicability of the method. The author considers the gravimetric determination with the apparatus of Fresenius preferable to the volumetric method.

He uses a potassa lye containing in 100 c.c. 35 grms. KOH. The aluminium is reduced to thin fragments with a file; they were put on a weighing-tube, about 1 grm. emptied into an Erlenmeyer flask holding about 150 c.c., and the weighing tube was re-weighed. Upon the aluminium there was poured a little water, and some vaseline added to prevent frothing.

The hydrogen evolved was burnt to form water in the apparatus of Fresenius, and the water was collected in concentrated sulphuric acid. In order to prevent too violent reaction and too rapid development of hydrogen, the potassa lye was added in small portions, proceeding otherwise according to the directions of Fresenius for the determination of zinc powder.

The solution went on regularly, and was completed in about 45 minutes. Towards the end, when the escape of gas became slow, heat was applied. In the flask there remains a brownish-grey solution, and a black undissolved residue.

The author purposes ascertaining whether this method is applicable to aluminium alloys (ferro-aluminium, aluminium bronze, &c.).—*Zeitschrift Analytische Chemie*, vol. xxix., p. 388.

THE DETECTION OF FOREIGN CRUDE PHOSPHATES IN GROUND BASIC SLAGS.

By L. BLUM.

THE superiority of basic slag as compared with other crude phosphates, on account of its being readily assimilated, is generally admitted. As a proof of this recognition we need only look at the rise in price which it has recently undergone. Along with this advance there has been a decline in the price of natural phosphates. Thus, in Lille, on May 10th, grey phosphatic chalk from Mons, finely ground, containing 40 to 45 per cent calcium phosphate, was quoted at 0.53 franc per unit of calcium phosphate per ton, which corresponds to a price of 0.11 franc per kilo. of phosphoric acid. It is, therefore, possible that these cheap, finely-ground, crude phosphates, may either be sold alone as basic slag, or may be mixed with slag meal, especially as they may serve to increase the percentage of phosphoric acid in inferior ground slags.

The question whether ground phosphates may be substituted for ground basic slag for manurial purposes with equal advantage has been much discussed of late. That opinion has been proved erroneous by the researches of P. Wagner and other chemists. These authorities have proved that it is not possible, even by the finest grinding to convert every undissolved phosphate into a sufficiently effective manure. An addition of such phosphates to basic slag involves loss to the purchaser, and the question is put to the analyst how may the presence of raw phosphates in basic slags be detected. The ordinary determination of phosphoric acid—the solution of the substance in a mineral acid and precipitation as ammonium phosphododekamolybdate, or its direct determination in an alkaline solution as magnesium-ammonium phosphate—exclude any such detection. It would therefore be necessary to treat basic slags on the citrate method like the “reverted” phosphates.

But if we compare the total composition of basic slags with that of crude native phosphates, inferences may be drawn which show the presence of the latter in ground basic slag. We may here remark that for this fraud only such phosphates will be used as are low in phosphoric acid, but rich in substances which waste sulphuric acid (so-called “profligate constituents”), e.g., calcium carbonate, and which consequently do not admit of remunerative conversion into superphosphate. For high grades of phosphates the makers of superphosphates pay so high a price per kilo. of phosphoric acid that the sophisticator would find no advantage in their employment.

Let us take as an instance the above mentioned grey phosphatic chalk of Mons. It contains 40 to 55 per cent calcium phosphate, about 50 per cent calcium carbonate, and consequently 22 per cent carbonic acid, little iron, and no manganese or mere traces. Recent pure basic slag contains no carbonic acid, and often considerable quantities of iron and manganese.

If ground basic slag is mixed with this ground phosphatic chalk the resulting mixture contains, according to the quantity of the addition, a large proportion of carbonic acid. In addition, the proportion of iron and manganese is reduced. We have, therefore, in the presence of carbonic acid in a basic slag an indication of the presence of foreign admixtures, since the preparation of basic slag completely excludes the presence of carbonic acid. Against this representation it may be objected that basic slag contains free lime, which greedily absorbs carbonic acid from the air, so that consequently basic slag meal, which has been lying for some time, contains a certain quantity of carbonic acid. It is also not impossible that the tetra-calcium phosphate in the slag may be decomposed by the carbonic acid of the air so as to form calcium carbonate. The objection is not unfounded, and the author has sought to throw light upon it by the following experiments. He determined the carbonic acid in various samples which were at hand. As there exist in the slags sulphides capable of decomposition by acids (CaS.MnS), he used in carrying out the determination the apparatus commonly employed for burning the carbon by means of chromic and sulphuric acid. As a mixture of both acids was used for decomposing the slags, it was certain that no sulphur compounds were obtained in the absorption apparatus. The quantities of carbonic acid obtained in this manner were as follows:—

1. Recent basic slag, not ground	0.00
2. Sample of commercial slag, finely ground	trace
3. Another sample, finely ground	0.16
4. Weathered slag which had been exposed for three years in the open air, finely ground	2.28
5. The same coarsely ground	2.18
6. The same; the portion intended for analysis was rubbed finely in an agate mortar, and remained for eight days exposed to the air of the laboratory, spread out in a thin layer on a sheet of paper	2.47

H. Otto (*Chemiker Zeitung*, vol. ii., p. 225), found in an analysis of basic slag which he there gives only a trace of carbonic acid. The sample used for experiment 6 lost on ignition 2.87 per cent. The excess of 0.40 per cent was due to moisture and combined water. In this case it may therefore be assumed with certainty that 2.47 per cent is the maximum of carbonic acid which the slag in question was able to take up. This maximum may certainly vary in any case according to the composition of the slag.

The inducement to this communication was the analysis of a ground basic slag, which along with the stipulated proportion of phosphoric acid contained 10.3 per cent of carbonic acid. I had no doubt that the slag had been falsified with an inferior ground native crude phosphate, rich in calcium carbonate.

Although the presence of foreign crude phosphates cannot be directly proved by the determination of carbonic acid we have here an easy method of deciding whether a slag-meal can be objected to in this respect. For this purpose it is sufficient to determine the loss of the dried sample on ignition. If this is too high there is *prima facie* ground to question the genuineness of the article.—*Zeitschrift Analytische Chemie*, vol. xxix., p. 408.)

DETERMINATION OF ASH IN MOLASSES, HONEY, &c.

By H. W. WILEY and HUBERT EDSON.

THE use of metallic silver prepared by reducing the chloride with an alkaline solution of grape sugar or by

direct reduction with iron or zinc, has been recommended as an aid in the oxidation of the carbon in the preparation of the ash from sugars, molasses, &c. The metallic silver acts as a carrier of oxygen, and after the completion of the reaction can be easily recovered from the ash by solution in nitric acid or otherwise.

Lucien* recommends the use of the oxide of zinc for this purpose. The oxide of zinc easily gives up its oxygen to the carbonaceous material, and is again easily oxidised in the muffle where the incineration takes place. At the end of the process, therefore, the ash is burned perfectly free from carbon and the zinc remains in the state of oxide. The weight of the ash can therefore be easily determined by deducting the weight of the oxide of zinc which has been added. The amount of oxide of zinc used, as recommended by Lucien, is 50 m.grms. to 2½ g. of molasses or 5 g. of sugar. Platinum dishes were used, and the platinum appeared to suffer no injurious effect from the action of the zinc.

We have given this method of ash determination a thorough trial, and the results are given in the accompanying tables.

First ash burned with ZnO, April 4. The sample and ZnO were thoroughly mixed together with H₂O.

The second and third samples of same date were mixed with alcohol, evaporated on steam bath, and residue incinerated. The ashes in both cases much improved in appearance by this treatment.

As will be seen from the above table, the mean percentage of ash in the samples of molasses used, when burned in the muffle in the usual way, was 8.04 per cent. In no case was the ash perfectly white. In the same

* *Bulletin de L'Association des Chimistes*, vi., p. 356.

Experiments on the Use of ZnO in Ash Determination. Sample of "Third" Molasses from Calumet Plantation, La.

TABLE No. 1. No ZnO Used.

Date	Weight sample.	Weight ash.	Per cent ash.	Remarks.
April 1	2.4614	0.1983	8.06	Ash rather dark.
" 1	3.4686	0.2810	8.17	" "
" 1	4.4886	0.3602	8.02	" "
" 3	2.4913	0.1997	8.01	Ash very slightly dark.
" 3	3.4904	0.2785	7.98	" nearly white.
" 3	4.4865	0.3591	8.00	" rather dark.
" 4	2.4877	0.2014	8.10	" quite dark.
" 4	3.4878	0.2785	7.99	" "
" 4	4.4931	0.3596	8.00	" "
Mean			8.04	

TABLE No. 2. ZnO Used.

Date	Weight sample.	Weight ash + ZnO.	Weight ZnO.	Weight ash.	Per cent ash.	Remarks.
April 1	2.4644	0.2453	0.05	0.1953	7.97	Ash white, better in appearance than without ZnO.
" 1	3.4865	0.3346	0.05	0.2846	8.17	Ash white, better in appearance than without ZnO.
" 1	4.4334	0.4083	0.05	0.3583	8.08	Ash white, better in appearance than without ZnO.
" 3	2.4904	0.2482	0.05	0.1982	7.96	Ash white, slightly better in appearance than without ZnO.
" 3	3.4955	0.3462	0.07	0.2762	7.90	Ash white, nearly same in appearance as corresponding ash without ZnO.
" 3	4.4847	0.4486	0.09	0.3586	8.00	Ash white, slightly better in appearance than without ZnO.
" 4	2.4926	0.2496	0.05	0.1996	8.01	Ash very white, much better in appearance than without ZnO.
" 4	3.4840	0.3425	0.07	0.2725	7.82	Ash very white, much better in appearance than without ZnO.
" 4	4.4805	0.4496	0.09	0.3596	8.03	Ash very white, much better in appearance than without ZnO.
Mean					7.99	

TABLE No. 3.

Date.	Loss ZnO.	Per cent ash. Corrected.
April 1	0'0015	8'21
" 1	0'0013	8'11
" 1	0'0030	8'08
" 3	0'0032	7'99
" 3	0'0032	8'07
" 3	0'0016	8'07
" 4	0'0021	7'88
" 4	0'0028	8'09
" 4	—	—
Mean	—	8'06

samples in comparative determinations, where oxide of zinc was used (Table No. 2) the mean percentage of ash was 7'99. The ash in all cases was very much improved in appearance, and apparently should have weighed much less than when no oxide of zinc was used. In the determinations made on the 4th of April, the zinc oxide was thoroughly mixed with the molasses by means of water or alcohol, while in the determinations made previous to that date it was simply sprinkled over the mass in the dish. The samples of ash obtained by previous mixing of the oxide with water or alcohol were very much whiter than any of the others. In order to determine whether there would be any loss from the ignition of the zinc oxide alone at the temperature used, a series of determinations was made, which showed an average loss of nearly 2 m.grms. for each 50 m.grms. of oxide employed. It is doubtful whether this loss takes place after the zinc oxide is thoroughly mixed with the sample, but in Table No. 3 the percentage of ash is given after correcting for the possible loss of zinc oxide. The mean percentage of ash as corrected in this way would be 8'06.

It is seen by the above work that for quantitative determination the numbers obtained with and without the zinc oxide are so nearly identical as to render its use of no particular value. If the ash is to be analysed quantitatively after it is obtained, the presence of the zinc would probably be of more injury than the trace of carbon which would remain without its use. We are therefore of the opinion that the method in ordinary use of determining the ash directly by carefully incinerating in the muffle, is to be preferred to the methods depending upon the admixture of any other substance to be used as a carrier of oxygen.—*Journal of Analytical Chemistry*, Vol. iii., Part 3.

A LECTURE EXPERIMENT.

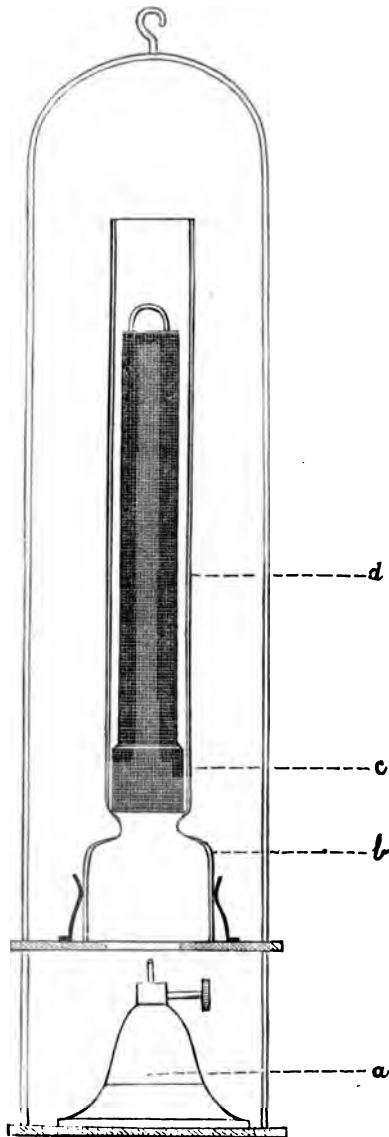
By SAVILLE SHAW, F.C.S.

THE following slight modification of a well-known lecture experiment may possibly prove of service to some of your readers.

The ordinary forms of apparatus for illustrating the indestructibility of matter by the increase in weight of a burning candle, have the disadvantage either of requiring the use of an aspirator, which is apt to draw the students' attention from the more essential part of the experiment, or in the modification, where the chimney itself contains the absorbing material, the draught is often uncertain, and a deposit of soot liable to occur and choke up the spaces between the lumps of soda-lime and caustic soda used.

Both these inconveniences are obviated by employing the apparatus shown in the figure, which consists of a small petroleum lamp, *a*, suspended in a wire framework beneath an ordinary lamp chimney, *b*, sufficient space being left to allow of the lamp being lighted without removal. The chimney contains a coil of coarse copper gauze, *c*, in the lower part of the narrow portion, above this is placed a rather open roll of iron gauze, *d*, provided with a handle of bent wire to facilitate its withdrawal, the roll being coated with caustic soda.

The covering of the gauze is easily performed either by dipping it in molten caustic contained in a nickel basin, or by ladling the melted substance over it.



The chimney may be removed from the apparatus and both ends closed by corks, enabling it to be used repeatedly without renewal. The gain in weight in three or four minutes amounts to about one gm., sufficient to show very appreciably on even a coarse lecture balance.

The Durham College of Science,
Newcastle-on-Tyne.

Micro-Organisms.—Messrs. Baillière, Tindall, and Cox will issue, in a few days, an octavo volume (360 pages and fifty-two figures), entitled, "Researches on Micro-Organisms," by Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c. The work is an *exposé* of recent researches in various branches of bacteriology, and includes an account of the distribution of microbes in air, soil, and water; animal alkaloids (ptomaines, &c.), soluble ferments, action of heat, light, and electricity on microbes; action of germicides, biology of microbes, &c.

THE ELECTROLYTIC METHOD APPLIED
TO MERCURY.

SEPARATION FROM COPPER.*

By EDGAR F. SMITH and LEE K. FRANKEL.

THE electrolytic precipitation of mercury has been successfully performed by different chemists; thus, J. B. Hannay (*Berichte d. d. Chem. Gesellschaft*, vi., 270) recommends a solution of mercury sulphate for this purpose, but gives no quantitative results. F. W. Clarke (*Am. Journal of Science*, xvi., 200; *Zeitschrift für Analyt. Chemie*, xviii., 103) separated mercury from the solution of its chloride, freely acidulated with sulphuric acid, by using a current obtained from six Bunsen chromic acid cells. Classen and Ludwig (*Berichte d. d. Chem. Gesellschaft*, xix., 323) employed a mercury solution rendered slightly acid with nitric acid, and a current affording 0.5 to 1.0 c.c. OH gas per minute. The time occupied in the deposition at ordinary temperatures was twelve to sixteen hours. Hoskinson (*Am. Chem. Journal*, viii., 209) obtained good results with the nitrate. Smith and Knerr

(*Am. Chem. Journal*, viii., 209) employed a nitrate solution, in which there was considerable acid in excess, and with a current yielding 4 c.c. OH gas per minute deposited 0.1 gm. of mercury in forty-five minutes. In all of these methods, which permit of the separation of mercury from many other metals, the mercury is thrown out as a mirror-like deposit, and drops of metal are plainly discernible.

We have observed that this metal can be separated without difficulty from solutions containing a large excess of alkaline cyanide, and with a comparatively weak current. The solution used was the chloride. The conditions, time, strength of current, and results are as follows, with mercury alone. (See Table I.)

The deposits in the determinations were compact, rather grey in colour, and showed in a few cases the drop-like nature so characteristic of mercury.

For washing purposes it was found best to use water only, because when this was followed with alcohol, we noticed that the latter detached thin films of metal, causing a loss in consequence.

The heat of the hand is sufficient to dry the deposit, though a warm iron plate may be used. Some of the deposits were allowed to dry slowly over sulphuric acid. In our experience, with about a hundred mercury depositions, we observed but five in which there was a slight oxidation of the metal. This only occurred when

* Read at the Stated Meeting of the Chemical Section of the Franklin Institute, April 16, 1889.

TABLE I.

Solution contained Hg. Grm.	Found Hg.	Per cent difference.	Quantity of KCN. Grms.	Total dilution. C.c.	Time in hours.	Current OH gas per minute. C.c.
0.1945	0.1953	+0.41	0.26	175	16	0.2
—	0.1948	+0.14	0.26	—	16	0.2
—	0.1946	+0.05	1.30	—	24	—
—	0.1930	-0.77	1.30	—	24	—
—	0.1945	—	1.30	—	12	0.2
—	0.1945	—	1.30	—	12	—
—	0.1945	—	2.60	—	12	0.2
—	0.1944	-0.05	0.65	—	12	—
—	0.1942	-0.14	0.65	—	12	0.2
—	0.1956	+0.56	0.65	—	12	0.2
—	0.1957	+0.61	1.30	—	12	—
—	0.1948	+0.14	1.30	—	12	0.2

TABLE III.

Hg present.	Hg found.	Difference in per cent.	KCN in grms. Grms.	Total dilution. C.c.	Current OH gas per minute. C.c.	Time in hours.
0.1833	0.1827	-0.27	1.5	200	2.8	16
—	0.1832	-0.05	1.5	200	2.8	16
—	0.1834	+0.05	1.5	200	2.8	16

TABLE IV.

Hg present.	Cu present. Per cent.	Hg found.	Difference. Per cent.	KCN. Grms.	Total dilution. C.c.	Current OH gas. per minute.	Time in hours.
0.1833	1	0.1821	-0.65	1.5	200	—	16
—	10	0.1828	-0.27	—	—	—	—
—	1	0.1821	-0.65	—	—	—	—
—	14	0.1833	—	—	—	—	—
—	10	0.1821	-0.65	—	—	—	—
—	5	0.1819	-0.76	—	—	—	—
—	3	0.1815	-0.98	—	—	—	—
—	5	0.1834	+0.05	—	—	—	—
—	3	0.1836	+0.16	—	—	—	—

TABLE V.

Ag present.	Copper.	Ag found.	Difference. Per cent.	KCN. Grms.	Current OH gas. C.c.	Time in hours.	Dilution.
0.1223	10	0.1257	+2.78	—	1	—	200
—	10	0.1299	+6.20	—	1	—	200
—	10	0.1225	+0.16	—	1	—	200
—	10	0.1263	+3.20	0.5	1	5	200
—	10	0.1257	+2.78	10	1	10	200
—	10	0.1244	+1.71	1.0	1	20	200
—	10	0.1251	+2.20	—	1	—	200
—	10	0.1242	+1.55	—	1	—	200

Copper precipi-
tated with silver.

a film of water remained in contact for some time with the deposited mercury.

In working with copper solutions, under conditions similar to those mentioned above, we discovered that this metal would not separate until the alkaline cyanide was completely decomposed. We therefore undertook a series of experiments with solutions containing both mercury and copper, hoping to effect their electrolytic separation. This seemed advisable, as the attempts in this direction had thus far not been as successful as might be desired (see Luckow, *Zeitschrift für analyt. Chem.*, viii., 24; and Classen, *Bericht d. d. Chem. Gesellschaft*, xvii., 2467; also *Zeitschrift für analyt. Chem.*, xxiv., 247).

Our mercury solution contained the same quantity of metal as in the first experiments. Seventy per cent of copper was added in each case. The quantity of cyanide varied from 0.65 grm. to 3.9 grms.; total dilution was 200 c.c., and the current strength varied from 0.1 to 0.4 c.c. OH gas per minute. Time, six to eighteen hours. Ten experiments were performed, and notwithstanding the mercury was completely deposited, slight quantities of copper were likewise thrown out of solution.

Thirty additional experiments were made; in each the quantity of mercury was 0.1945 grm., while the copper varied from 14 to 70 per cent. The quantity of alkaline cyanide varied from 3.9 to 8.5 grms.; total dilution remained 200 c.c. The current averaged 0.4 to 0.12 c.c. OH gas per minute. Time, eighteen hours. The best results were these:—

Hg taken. Grm.	Hg found.	Difference in per cent.
0.1945	0.1932	-0.66
—	0.1920	-1.28
—	0.1927	-0.92
—	0.1936	-0.46
—	0.1930	-0.77
—	0.1936	-0.46
—	0.1954	+0.46
—	0.1938	-0.36
—	0.1923	-1.13
—	0.1921	-1.23

These, as well as the results obtained in twenty experiments made later, seem to indicate that the presence of the copper exercises considerable influence upon the precipitation of the mercury—retards it. This fact, we think, was confirmed by ten or more experiments, in all of which a slight quantity of the mercury was retained in solution, notwithstanding the current was increased to 1.2 c.c. OH gas per minute, and the amount of cyanide considerably reduced. The time of each precipitation was continued through seventeen hours.

Our attention was next directed to ascertaining whether or not a stronger current might be used to throw out the mercury, and at the same time leave the copper in solution. The results with mercury alone are given in Table III.

Using the same quantity of mercury and varying amounts of copper the results were as follows. (See Table IV.). These results are recorded in the order obtained, while the differences in percentage from that required vary from +0.05 to -0.98 per cent, and in six cases out of nine show a deficiency in the mercury, yet a careful qualitative examination of each filtrate failed to detect this metal; the error must therefore be ascribed to other causes. It may not be improper to add that these determinations and separations were not always conducted in the same platinum vessels, and, further, those used by us ranged in weight from 61 to 135 grms.

Where the quantity of copper exceeded 20 per cent of the mercury, the results were unsatisfactory.

It is well known that silver can be separated qualitatively from its cyanide solution, but whether its separation from copper could be effected in the same manner as

that by which mercury and copper were separated was undetermined; to ascertain this, we made forty experiments; ten of which resulted as follows. (See Table V.)

Later, we diminish the quantity of copper, with no better results. On increasing the quantity of cyanide, and also the strength of the current, the silver was very notably retarded in its deposition. After carefully repeating the work with no better outcome, we feel justified in saying that the cyanide method cannot be applied in the electrolytic separation of these two metals.

The current employed by us was obtained from storage batteries of the Julien form. Each cell contains nineteen plates, each of which is five and three-quarter inches square. In a long experience, with almost every form of battery, in electrolytic work, we have not had the same even steady current for a series of hours as with the Julien form, and recommend it to all engaged in similar experiments. See, further, *Berichte d. d. chem. Gesellschaft*, xxi., 2892.

ON THE SO-CALLED PEROFSKITE FROM MAGNET COVE, ARKANSAS.

By F. W. MAR.

In 1877 it was shown by Knop* that the supposed perovskite of the Kaiserstuhl, contained besides titanium a considerable amount (23 per cent) of niobium and tantalum, and he accordingly made it an independent species and named it very appropriately *Dysanallyte*. The analysis of the similar mineral from Magnet Cove, Arkansas, the results of which are given below, shows that it is also distinct from perovskite, and is to be classed with dysanallyte. For the material for analysis I am indebted to the kindness of Professor E. S. Dana.

The method of analysis was as follows:—0.500 grm. of the carefully selected mineral was placed with about 15 c.m.³ of concentrated sulphuric acid in a platinum crucible of 150 c.m.³ capacity, and the whole being covered with a watch-glass that the progress of the decomposition might be easily observed, boiled for ten or fifteen minutes. The cooled product was poured into 600 or 700 c.m.³ of cold water and allowed to stand over night or until the calcium sulphate was completely dissolved. A small residue was usually found, and this was put through the same process. Any final residue is silica and sometimes a little tantalum or niobium oxide. The former was determined by evaporation with sulphuric and hydrofluoric acids and the remaining oxide was added to the main oxides.

The solution of the mineral was then made slightly alkaline with ammonia, and the precipitated earth filtered off. The lime was thrown out of the concentrated filtrate as oxalate, and after evaporation and volatilisation of ammonia salts, magnesia was determined in the residue. Alkalies should be found at this point if present; there were none.

The weighed earths obtained as above were fused in sodium carbonate, enough sulphuric acid added to the mass to bring about a bisulphate fusion, and then enough more to keep the whole in the liquid condition even when cold. After cooling, the mass was poured into 300 c.m.³ of cold water containing 1 grm. of tartaric acid, and after separating the iron in alkaline solution by hydric sulphide the titanium, with which go the niobium and tantalum, were separated by the acetic acid process of Professor Gooch.† The greater part of the manganese was separated by an ordinary acetate process, and the acid oxides by the strong acetate process. On neutralising the filtrate from this last with ammonia and boiling, only

* *Zeitschr. für Kryst.*, i., 284, 1877.

† "Proceedings Amer. Acad. of Arts and Sci.," N.S., vol. xii., p. 435

		Molec. Ratio.	Quantiv. Ratio.	
CaO..	33.22	÷ 56 = 0.593	0.611 or 23 × 2 1.22	= 4
MgO ..	0.74	÷ 40 = 0.018		
FeO..	0.23	Fe ₂ O ₄	1.52 or 3	
	0.50			
Fe ₂ O ₃	5.66	÷ 160 = 0.035	0.050 or 2 × 6 0.300	= 1
[Yt, Er, Tr] ₂ O ₃ ..	5.42	428 = 0.012		
[Ce, La, Di] ₂ O ₃ ..	0.10	328 = 0.003	0.027 or 1 × 10 0.270	= 1
Ta ₂ O ₅ ..	4.38	268 = 0.016		
Nb ₂ O ₅ ..	5.08	444 = 0.011	0.539 or 20 × 4 2.156	= 7
TiO ₃ ..	44.12	82 = 0.538		
SiO ₂ ..	0.08	60 = 0.001		

99.53

a trace of some earth was found showing absence of alumina. The titanium was separated from the weighed oxides by Knop's chlorinating process, and finally the niobium was determined in the mixture of niobium and tantalum oxides by reduction in hydrochloric acid and titration with permanganate after T. B. Osborne.* Only a trace of titanium was found in the niobium and tantalum oxides by the Osborne process with hydrogen peroxides, and the titanium re-estimated by the same process gave practically the same result as before.

A portion of the oxides having been lost during the operation, having gone, as it appeared, with the manganese used to decompose the tartaric acid, another portion of mineral was treated in the same manner as far as this point, and the tartaric acid was destroyed by evaporation in platinum and ignition. No aluminum having been found, the titanium, tantalum, and niobium oxides were separated by boiling with dilute sulphuric acid. By evaporation of this filtrate a quantity of earths was obtained. To this was added another portion separated by ammonia from the filtrate (in the same portion of mineral) after separation of lime, evaporation and ignition, and solution in hydrochloric acid, and before the precipitation of the magnesia by microcosmic salt. The combined earths were precipitated in a slightly acid solution by oxalic acid in order to separate from any uranium, the cerium and yttrium groups separated by the sodium sulphate process, and each precipitated again as oxalate and weighed as oxide. As appears the main portion of the rarer earths belongs to the yttrium group.

An attempt was made to take the atomic weight, but the result obtained, 190, is probably too high, the colour showing that part of the sulphate was changed to a basic salt. This, however, with the colour of the oxides, a reddish brown, and the fact that the solutions do not yield an absorption spectrum, suggests that a chief portion of the earth is terbium oxide.

The result of the analysis is given in the Table.

Specific gravity = 4.18.

In conclusion I would express my thanks to Professor Gooch, of the Kent Laboratory, for the valuable advice and assistance freely given by him during the course of the analysis.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION OF GREAT BRITAIN.
General Monthly Meeting, November 3, 1890.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following were elected Members of the Royal Institution:—Viriamu Jones, M.A.; C. N. Nicholson, M.A.; John Hartley Perks, J.P.; The Hon. Sir James Stirling.

* *Amer. Chem. Journ.*, vol. xxx., p. 329.

The special thanks of the Members were returned to Dr. J. A. Fleming for the presentation on behalf of Professor Elihu Thomson of the Apparatus employed by Prof. Thomson in his experiments on Electro-magnetic Repulsion; and to Hervey Pechell for his present of an old engraving (1809) of the Library of the Royal Institution.

The Managers reported that at their meeting held this day they had elected Victor Horsley, F.R.S., Fullerian Professor of Physiology for three years (the appointment dating from January 12, 1891).

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Sugar Analysis; for Refineries, Sugar-houses, Experimental Stations, &c., and as a Handbook of Instruction in Schools of Chemical Technology. By FERDINAND G. WIECHMANN, Ph.D. New York: John Wiley and Sons, 1890. 8vo., pp. viii.—187.

THIS admirable volume is the result of the author's experience as consulting chemist to the extensive sugar refining company of the Messrs. Havemeyers and Elder, Brooklyn, N.Y. Its aim is to supply the practical sugar-chemist with a concise and thorough treatise embodying the new methods of analysis that are so widely scattered throughout periodical literature. The author, being at the same time Instructor in Chemical Philosophy, School of Mines, Columbia College, has arranged the material in such a way that the work can be used for elementary instruction in this branch of analytical chemistry. Instead of describing in turn the different products met with in laboratory work, such as raw sugars, liquors, molasses, &c., the author deals with the individual constituents, as sucrose, invert-sugar, ash, water, &c., and thus avoids repetitions.

The volume opens with a discussion of polarisation, and the various instruments of precision used in sugar-analysis; it continues with the methods employed, introducing examples where feasible. A brief bibliography is given, but unfortunately the places of publication and dates of the issue are omitted.

The tables, nineteen in number, conclude a practical and useful work abreast of modern requirements. The table of English, French, and German synonyms on pages 108—109 is valuable, and rather a suggestive feature. We note the clear type and the index.

Republic of Uruguay. International Exhibition of Mining and Metallurgy, Crystal Palace, London, 1889.

WE have here, in the first place, a catalogue of minerals from the museum of the Consulate General of Uruguay. There are specimens of gold, silver, copper, and iron, pyrites being described as very common. Platinum, tin,

mercury, and cobalt are said to occur, though no specimens were shown at last year's Exhibition. The silver ore of Uruguay contains, according to Lettson, 87 per cent of fine silver. There are also copper ores at 56 per cent and magnetic iron ore at 72 per cent. Agates, rock-crystals, marbles, and even diamonds and topaz, have also been found. "Calcareous cement" occurs on the left shores of the Brujas, and on the sides of the Gerro of Monte Video.

The pamphlet further contains the mining-laws of Uruguay, summed up in 182 sections, and a map of the republic.

Griffin's Scientific Text-Books. A Treatise on Electro-Metallurgy; Embracing the Application of Electrolysis to the Plating, Depositing, Smelting, and Refining of various Metals, and to the Reproduction of Printing Surfaces and Art-Work. By W. G. McMILLAN, F.I.C., F.C.S. London: C. Griffin and Co.

LIKE not a few other technical monographs, this treatise is to some extent encumbered with matter for which the reader might have been quite as well referred to any of the multitudinous chemical and physical treatises which have been lately issued. The work before us does not differ very widely from that by A. Watt on the "Electro-Deposition of Metals." It is, perhaps, somewhat more comprehensive in its plan, but in some departments, at least, it goes less into detail.

As regards the early history of the art, Mr. McMillan considers it a "hopeless task to determine the question of real priority between the three inventors." Watt distinctly awards the palm to Jordan. In the work before us we find a table of the atomic weights of the elements, in which that of platinum is still given as higher than that of gold. We regret to find also that the author ignores the hydrometer scale of Twaddle and brings forward that of Baumé, which is ambiguous, as it exists in two, if not three, modifications. Further a reading on Baumé's scale cannot be at once reduced to direct specific gravity of a simple calculation, as can that of Twaddle.

The processes mentioned in Mr. McMillan's work are described with great clearness, and the operator is duly cautioned on the necessity of cleanliness in apparatus, in materials, work-tables, and in the air of rooms.

The working material of the electro-metallurgist, which has now assumed a considerable extent, is here given in full, and operators are duly cautioned against the poisonous nature of many of the articles. There is a salutary warning against putting such solutions in tumblers, wine-glasses, &c. A still better precaution is never to bring any article of food or drink into laboratories or workshops where poisons are stored or employed.

The work before us may be regarded as decidedly satisfactory both in plan and execution.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—It is impossible for us to communicate individually with the hundreds of Fellows of the Chemical Society who have signed and returned the circular issued by us relating to the present method of election of Fellows, we therefore ask that you will permit us to make the following facts known through your columns.

The Committee have addressed a letter to the President and Council of the Chemical Society, enclosing a copy of the said circular, thus formally placing the recommendations contained therein before the Council.

In addition the Committee have thought it right to forward a summary of the numerous further suggestions

which have been sent to them, some of which, it is hoped, may be finally adopted. We have expressed the hope that the Council will give the matter their immediate consideration. We have no doubt the Council will recognise the expressed opinions of a large proportion of the Fellows and give our letter a favourable reply. Meantime we shall be glad to receive the circular from any Fellow who may have delayed signing the same.—We are, &c.,

FREDK. J. LLOYD. } Hon.
FRANK L. TEED. } Secs.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—While the correspondence is going on through the CHEMICAL NEWS about the Chemical Society, may I be allowed to say a word about the Institute of Chemistry?

Before one is allowed to take the examination for qualification as a "Fellow," he has to show proof of having attended a College for a three years' course in science (colleges named by the Institute).

Now there are a great many who have not had that opportunity, but who are quite qualified to pass the examination set by the Institute, even better than many who have had the college training, and who would perhaps be more useful to that body.

Would it not be more just to give the outsiders a chance of becoming "Fellows?"—I am, &c.,

"CHEMICAL."

THE PREVALENCE OF COPPER IN CEREALS.

To the Editor of the Chemical News.

SIR,—The occasional existence of copper in cereals, peas, beans, &c., as a natural constituent has long been known, but as the question is a very important one, especially in this country, where copper is looked upon as an article highly injurious to health, no apology is necessary from me for drawing the attention of your readers to the subject.

The question has very lately been prominently brought under my observation, and that in a novel and unexpected manner, necessitating the examination of a large number of samples of wheat and barley, which resulted in 15 per cent of the samples being found to contain copper in more or less quantity, particularly in the Scotch barley.

The existence of copper in cereals therefore becomes a serious question, especially to manufacturers of infants' foods, as they are liable at any moment to have proceedings instituted against them under the Sale of Food and Drugs Act. It was due to legal proceedings being threatened against a manufacturer of infants' food which caused the matter to be placed in my hands. The plaintiff's analyst certified that the food contained lead, which had caused serious illness to an infant. But upon closer investigation by myself it proved to be copper, and it was present there as a natural constituent of one of the cereals used in the preparation of that particular infants' food.

Granting that cereals do possess the remarkable property of taking up copper from the soils in which they are grown, provided that soil contains copper, the question immediately arises: What is the maximum quantity which barley or wheat are capable of taking up?

Few soils in this country contain copper to any appreciable extent. I am therefore inclined to attribute the presence of copper in Scotch barley and English wheat to the prevalent practice of dressing the grain and also the ground with sulphate of copper, so as to protect it from the ravages of vermin after the grain is sown.

The possible existence of copper in cereals may also account for some of those mysterious and unaccountable cases of illness which occur from time to time in families, and is therefore well worth the medical practitioner's

attention, and also the manufacturers of infants' food.—I am, &c.,

WILLIAM JOHNSTONE.

13, Fish Street Hill, E.C.

INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

To the Editor of the Chemical News.

SIR,—In the account published in the CHEMICAL NEWS (vol. lxii., pp. 218 and 227) of the work of the American Committee upon the International Standards for the Analysis of Iron and Steel will be found a statement, well supported by experimental evidence, to the effect that the ordinary chloride of ammonium and copper contains some soluble carbonaceous constituent which is precipitated to some extent when steel is dissolved in it, thereby raising the apparent percentage of carbon in the metal. An hypothesis is put forward that this constituent is cellulose.

Attempts have been made to free the double chloride from such impurity, but not with complete success. These attempts have consisted in repeated re-crystallisations, and have not included endeavours to start with the ultimate constituents of the double salt free from organic impurity, and thus obtain a product of which the history and mode of preparation would be accurately known.

I am at the disadvantage of not having access to the original report at the time of writing, and therefore what I am about to say may be anticipated by statements not appearing in the abstract; but, premising that such is not the case, I would respectfully suggest to the Committee that by far the most satisfactory method of settling the whole question would be to prepare pure ammonio cupric chloride from pure metallic copper and hydrochloric and nitric acids and ammonia re-distilled in the laboratory. Then, provided the operations were performed with careful exclusion of dust, there should be no doubt as to the freedom of the resulting product from organic matter. This is so obvious a course, that it has doubtless received the consideration of the Committee, and my reason in writing is to ascertain wherein it has been found wanting.—I am, &c.,

BERTRAM BLOUNT.

Laboratory, Broadway, Westminster, S.W.,
November 10, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

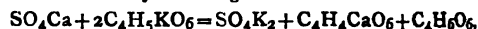
Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 16, October 20, 1890.

Researches on the Equivalent of Fluorine.—Henri Moissan.—The author remarks that Berzelius and Dumas, in determining the equivalent of fluorine, made use chiefly of mineral specimens of fluor-spar, as pure as possible. It may always be feared that such specimens may contain traces of silica or of phosphorus, as it has been shown by Berzelius and Louget. The author has therefore used synthetic calcium fluoride, distinctly crystallised. From his experiments, made with sodium and calcium fluorides, he finds the equivalent of fluorine = 19.05.

Action of the Aromatic Amines and of Phenylhydrazine upon the β -Ketonic Nitriles.—L. Bourcault.—The author, referring to a former memoir by M. Hanriot and himself, showing that methylpropionylacetone nitrile condenses with certain aromatic amines and phenylhydrazine with elimination of a mol. of water. He

now gives his results on the constitution of these compounds.

On the Manner of Combination of the Sulphuric Acid in "Plastered" Wines, and on a Method of Analysis rendering it possible to distinguish "Plastering" from Acidification with Sulphuric Acid.—L. Roos and E. Thomas.—The authors admit the equation proposed by MM. Bérard, Chancel, and Canvy, and afterwards by Dr. Magnier de la Source—



but they give a different interpretation to the secondary reaction, which occasions the presence of free tartaric acid. They maintain that this acid acts by preference on those organic compounds with a potassium base which, as Dr. Magnier de la Source has demonstrated, exist in wine in a notable proportion. The addition to wine of a little tartaric acid doubles the quantity of tartar which may be extracted from it. The analytical process adopted by the authors is as follows:—(a). Determine the chlorine present in the sample by the ordinary method. (b). Determine total sulphuric acid. (c). In 50 c.c. of the wine, mixed with a few drops of ammonium acetate, precipitate all the sulphuric acid as determined by the determination (b), with an absolutely exact quantity of barium chloride in a standard solution. (d). Determine chloride in the filtrate from operation (c). If we have to do with a neutral potassium sulphate all the chlorine of the barium chloride will be found in the state of potassium chloride. If we have an acid sulphate, hydrochloric acid (or ammonium hydrochlorate) will be set free, and will disappear during the slight ignition which precedes the determination (d) with standard silver solution, there being always a proportional loss of chlorine.

On Saccharine Matters in Mushrooms.—Em. Bourquelot.—Vegetable transformations go on in mushrooms even after they are gathered, and may in a few hours affect the disappearance of trehalose and the production of mannite. The author has therefore taken the precaution of plunging his mushrooms into boiling water immediately when gathered, so as to arrest all change. All the species, except *Amahita mappa*, if examined when young, contained exclusively trehalose. When older, they contain both trehalose and mannite, or mannite alone. In two species which were examined after desiccation at a low temperature (*Bolletus aurantiacus* and *Hypholoma fasciculare*) the trehalose had disappeared and was replaced by mannite.

Bulletin de la Société Chimique de Paris.

Series 3, Vol. iv., No. 1.

The Influence of the Different Fruit Ferments upon the Bouquet of Fermented Liquors on the Production of a Barley Cider.—Georges Jacquemin.—Already noticed.

Action of Lead Oxide upon Toluene. Production of Benzene.—C. Vincent.—Behr and Van Dorp let fall toluene drop by drop upon lead oxide heated to dull redness. The crude product being distilled to separate the unattacked toluene, the stilbene was crystallised in alcohol, whilst the diphenyl, the phenanthrene, the anthracene, and an oily hydrocarbon remain in solution in the alcohol. The author has resumed the study of this reaction upon toluene, under the same conditions, using pure toluene exempt from benzene. This reaction may be industrially utilised to transform a lot of toluene for which there is no demand into benzene, which is more valuable. The chief facts established in the paper are that lead oxide attacks pure toluene at a temperature below 335°, producing chiefly water, carbonic acid, and benzene. At higher temperatures, we obtain less benzene, more stilbene, and higher carbides. At dull redness, there are produced, along with the products above mentioned, the

carbides which are formed by the simple pyrogenous decomposition of benzene and toluene. The diphenyl, which appears in small quantities in this operation, does not come from the benzene originally contained in the toluene, but from the benzene formed by the action of lead oxide upon the toluene itself.

On Tetrachlorophenol.—Louis Hugounenq.—This compound is obtained by saponifying tetrachloroanisole with hydriodic acid at 1:7. The product, $C_6HCl_4.OH$, crystallises in white needles, fusible, if pure, at 152° . It is insoluble in water, very soluble in all the organic solvents, and capable of sublimation. It boils with decomposition at 278° ; its odour is peculiar, its taste caustic. The alcoholic solution behaves as an acid with indicators, and decomposes carbonates. The author has examined its ammonium, silver, lead, and copper salts.

Researches on Dispersion in Organic Compounds (Alcohols of the Fatty Series).—Ph. Barbier and L. Roux.—In the alcohols of the fatty series which the authors have examined, the dispersive powers are continuous functions of the molecular weights; and, contrary to what is observed in the aromatic compounds, they increase simultaneously with the molecular weights. Alcohols with a long chain, primary or secondary, have the same dispersive power, and follow the same laws; only the two primary abnormal alcohols (the isobutylic and isoamyl) possess lower dispersive powers, though their values do not deviate very notably from those of the alcohols with a long chain. In this series, as in that of the aromatic compounds, the elimination of the hydrogen determines a considerable increase in the dispersive power.

On Manganese Oxides obtained in the Moist Way.—A. Gorgeu.—The author studies manganous acids, describing nine methods for its preparation. He considers the two processes for obtaining manganous anhydride, and explains the properties of manganous acid, its behaviour with hydrate dioxides, and with metallic salts. The author raises the question whether the synthesis of potassium manganate does not result from the oxidation of manganous acid at the expense of potassium permanganate. He holds that the fact of the splitting up of manganic acid by water into two compounds, MnO_2 , Mn_2O_3 , the one richer and the other poorer in oxygen than the original acid, and without any escape of gas, is a fact which has been observed only in the case of osmious acid.

A New Biethylenic Carbide, β -Bipropylene.—F. Couturier.—This compound is formed by the elimination of 2 mols. of water from pinacone. Its composition is C_6H_{10} .

Journal de Pharmacie et de Chimie.
Series 5, Vol. xxi., No. 7.

Researches on the Preparation and the Properties of Aricine.—H. Moissan and Ed. Landrin.—The composition of aricine is expressed by the formula $C_{23}H_{26}N_2O_4$. Its rotatory power in an alcoholic solution is $\alpha_D = -58^\circ 18'$. In an ethereal solution it gives the figure $\alpha_D = -92^\circ 30'$. The hydrochloric solution has generally been regarded as inactive, but it possesses a rotatory power contrary to that of the alkaloid $\alpha_D = +14^\circ 30'$.

Action of Time on Coal-Tar Colours in Wines.—M. Monaron.—The author proves experimentally that a wine coloured with acid magenta preserves all its characters for a long time if protected from microscopic vegetation.

Reduction of Silver Nitrate by Oil of Bitter Almonds.—E. Le Noble.—This reduction takes place under a variety of conditions. The author concludes that benzoyl hydride behaves like the aldehyds, reducing silver oxide, and passing to the state of benzoic acid.

Determination of Total Phosphorus in Urine.—M. Chappelle.—The author heats 10 c.c. of urine with 5 c.c. of sulphuric acid for several hours until it becomes colourless. The liquid is made up with water to 50 c.c., neutralised with soda and treated with magnesia mixture. The determination is then completed in the ordinary manner.

The Analysis of Commercial Glycerins.—M. Vignier.—The only processes for the determination of glycerin in an accurate manner are the method of Benedikt (conversion of the glycerin into triacetate), and that of Hehner (decomposition of glycerin by potassium dichromate). It is, however, pretended by dealers that a crude glycerin containing not less than 80 per cent of pure glycerin should have a specific gravity of not less than 1.300 (at 15°) and a boiling point not below 155° . The author finds experimentally that there is no definite relation between the proportion of actual glycerin in a sample and its specific gravity and its boiling point. It is not possible to ascertain the value of a crude glycerin by its specific gravity and its boiling point.

Distinguishing Characters of Vanillin and Coniferin.—A. de Werre.—With sulphuric acid vanillin gives a yellow colour and coniferin a violet. With a mixture of sulphuric acid and resorcinic vanillin gives a deep carmine red, and coniferin a violet; phloroglucin and hydrochloric acid vanillin gives a red colour, whilst coniferin yields only a very fugitive violet.

Detection of Mercury in Urine and Organic Liquids.—E. Brugnatelli (*Annali di Chimica*).—The author acidifies the suspected liquid with a few drops of hydrochloric acid, adds powdered copper or copper wire well cleansed and reduced to redness, heats for five minutes in the water-bath to 50 to 60° , stirring occasionally, washes the copper, places it in a capsule, and along with it a fragment of porcelain on which is placed a drop of solution of gold chloride at 1 per cent. The capsule is covered and heated on the water-bath; the mercury deposited on the copper is volatilised and reduces the gold.

Excretion of Creatinin during Fasting and its Formation in the Organism.—Dario Baldi.—The author found in the urine of the fasting exhibitor, Succi, 0.40 grm. of creatinin on the seventeenth day of the fast and traces on the twenty-third day. He considers this observation a proof that creatinin is an ultimate product of the organic transformations.

Artificial Musk.—A. Baur.—The author obtains this substance by the nitration of isobutyltoluene. It is a solid substance, crystallising in small white laminae of the pure odour of natural musk and of an extraordinary intensity. The process has, of course, been patented and sold to certain perfumers who are manufacturing the perfume at Mulhouse. The musk-deer may therefore be considered as disestablished.

Determination of Ferric Oxide and Alumina in Phosphates.—E. Glaser.—The author dissolves 5 grms. of the phosphate in 25 c.c. of nitric acid of sp. gr. 1.2 and 12.5 c.c. of hydrochloric acid at sp. gr. 1.12, and dilutes to half a litre. He introduces 100 c.c. of the solution (corresponding to 1 grm. of the substance, into a quarter-litre flask and adds 25 c.c. of sulphuric acid at 1.84. It is let settle for five minutes, stirred repeatedly, 100 c.c. of alcohol at 95 per cent are added, the flask is cooled, filled up with alcohol, and well shaken. The stopper is withdrawn, and alcohol is added up to the mark (as contraction will have taken place), and the flask is again shaken. After standing for half-an-hour it is filtered; 100 c.c. (representing 0.4 grm. of the original substance) are evaporated in a platinum capsule so as to expel all the alcohol. To the liquid thus freed from alcohol there are then added in a glass vessel 50 c.c. of water, and it is heated to a boil. It is then removed from the source of heat, and ammonia is added until the reaction is alkaline.

The excess of ammonia is driven off by boiling, the liquid is let cool, filtered, washed with hot water, heated to redness, and the iron and aluminium phosphates are weighed.

Manufacture of Aluminium.—C. Nello.—In this paper, taken from the *Zeitschrift für angewandte Chemie*, the author gives an account of the manufacture of aluminium from cryolite, as carried on by the Alliance Aluminium Company.

Chemical Bibliography.—E. Fremy.—The author writes as follows:—"The chemists of the so-called modern school, wishing, mistakenly, to combat the admirable theories of Lavoisier, and to give an exaggerated extension to observations made on the influence of water in certain salts, have maintained that when an acid loses its water and becomes anhydrous, it is no longer an acid; they have given to dehydrated acids the name of anhydrides. The object of this theory is to maintain that a salt is not a compound of acid and of base, but a substitution of the hydrogen of the acid by a metal. I believe I have demonstrated that this theory ought to be absolutely rejected by citing thousands of salts which are produced by the combination of anhydrous acids with anhydrous bases, such as the carbonates, silicates, borates, aluminates, stannates, &c. In all these cases the acid being anhydrous, the phenomenon of substitution has no place; it is the anhydrous acid which combines with the anhydrous base, as the theory of Lavoisier demands."

No. 8.

On the Precipitate formed in Solutions of Copper Sulphate in Common Water.—MM. Grimbart and Barré.—If a solution of copper sulphate is poured into common water there is first produced an intense turbidity, then, on standing, a voluminous greenish-blue deposit of a crystalline aspect forms at the bottom of the vessel. This compound is a quadribasic sulphate, similar in composition to the mineral brochantite found in Mexico and Iceland. Its formation is probably due to the calcium bicarbonate present in ordinary waters.

Rapid Determination of Chlorides in Wines.—M. L. Roos.—The author prepares two standard solutions, one of silver nitrate at 5 per cent and the other of potassium ferrocyanide, which must saturate each other exactly. The so-called decimal solutions are perfectly suitable. To 20 c.c. of wine he adds an excess of the silver solution, and then he determines with the ferrocyanide the quantity of silver not taken up by the chlorine. The ferrocyanide is added by degrees, making from time to time spot-tests on filter-paper, and adding to each spot a small drop of solution of ferrous sulphate. The spot remains red as long as there is not an excess of ferrocyanide, and becomes distinctly blue as soon as the saturation is exceeded. The author admits that this procedure is not as precise as the ordinary method with silver nitrate and potassium chromate as indicator.

The Presence in Urine of some Substances which Reduce Copper Oxide on Boiling in presence of an Alkali.—H. Ashdown.—From the *Pharmaceutical Journal*.

Researches on the Pathogenic Microbia of the Filtered Waters of the Rhone.—MM. Lortet and Despeigner.—The drinking water supplied to the public of Lyon is taken above the city and filtered in galleries separated from the river by a bed of fresh gravel of the mean thickness of 15 metres. The subterranean chambers are walled on their four sides and filter only through the bottom. It appears from a bacteriological analysis published in 1886 that the free water of the river, opposite this installation contain 51,000 germs per litre. That taken in the filtering galleries contain only about 7000. Notwithstanding this purification these waters deposit quickly upon the Chamberland filters an unctuous, slimy mud, coloured deeply yellow by ferric oxide and formed of a fine marl along with organic matter. Under the microscope this deposit is found swarming with bacteria of

different forms, some of which when injected into guinea-pigs have occasioned various diseases.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Nickel Capsules.—I shall be greatly obliged to any of your readers who can inform me, through your columns, as to their experience with the nickel capsules that have lately been introduced to the notice of chemists. I am anxious to know how far they may replace platinum in ordinary analytical work; and whether, in fact, they can be recommended as generally satisfactory apparatus.—C.

MEETINGS FOR THE WEEK.

WEDNESDAY, 19th.—Society of Arts, 8. Opening Address of the 137th Session, by the Attorney-General, Sir Richard Webster, M.P. (Chairman of the Council of the Society).

THURSDAY, 20th.—Chemical 8. Ballot for the Election of Fellows. "On the Estimation of Cane-sugar," by C. O'Sullivan and F. W. Thompson. "A New Method of Determining the Specific Volumes of Liquids and of their Saturated Vapours," by S. Young. "The Molecular Weight of Metals when in Solution," by Messrs. Haycock and Neville.

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TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive TENDERS for the SUPPLY of 1000 tons of SULPHURIC ACID.

Deliveries to be made in bulk at the Northern and Southern Outfalls, and in carboys to Stations within the Metropolis, commencing about the 1st May next.

Persons tendering will be required to declare in their tender that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council, at the Office, 40, Craven Street, W.C., until Saturday, the 22nd November, 1890. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., endorsed "Tender for Sulphuric Acid," and be sent in not later than 5 o'clock on Monday afternoon, the 24th of November, 1890.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE, Clerk of the Council.

Spring Gardens,
3rd November, 1890.

TO MANUFACTURING CHEMISTS AND OTHERS.

THE LONDON COUNTY COUNCIL is prepared to receive TENDERS for the SUPPLY of 1300 TONS of MANGANATE OF SODA, to be delivered at the rate of not less than 50 tons nor more than 200 tons per week, from the 1st March, 1891.

Persons tendering will be required to declare in their tender that they pay such rates of wages and observe such hours of labour as are generally accepted as fair in the trade.

The Specification, Form of Tender, and other particulars may be obtained on application to the Chemist of the Council, at the office, 40, Craven Street, W.C., until Saturday, the 22nd November, 1890. Tenders must be addressed to the Clerk of the London County Council, Spring Gardens, London, S.W., endorsed "Tender for Manganate," and be sent in not later than 5 o'clock on Monday afternoon, the 24th November, 1890.

The Council does not bind itself to accept the lowest or any tender.

H. DE LA HOOKE, Clerk of the Council.

Spring Gardens,
3rd November, 1890.

THE CHEMICAL NEWS.

VOL. LXII. No. 1617.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

BEFORE proceeding further with the analysis of mixtures of oils, I give a list of oils, &c., on which I have operated. The first division contains those which yield insoluble products with sulphur chloride; the oils contained in the second division do not yield such products, hence the oils of the first division can be separated from those of the second.

The oils, &c., of the first division, when heated strongly with sulphur, yield spongy elastic masses, except the oils of olive and cotton-seed, hence these oils may be separated from the others; the sulphur which they dissolve separates out on cooling, which may help to recognise their presence in a mixture. They all dissolve in ether, but, on addition of a few drops of alcohol, caoutchouc and gutta-percha separate out.

First Division.

Olive oil.	Walnut, decort.
Olive oil from green olives.	Sesame.
Olive oil from kernels of green olives.	Nigerseed.
Poppy oil, var. :—	Castor oil.
Papav., somnif.	Rapeseed.
Glaucium flav.	" blown.
Almond, var. :—	Cotton oil.
Amygd., dulc.	" crude.
" amar.	" blown.
Earthnut.	Beechmast.
" decort.	Hempseed.
Caoutchouc, gutta-percha, and allied substances. . .	And the resins naturally associated with them.

Second Division.

Petroleum and Homologues of the Paraffin Series. Distillates from Coal-Tar, Shale, and similar Minerals.

Sperm oil.	Beef fat.
Whale oil.	Mutton fat.
Cod oil.	Cocoanut oil.
Spermaceti.	Palm oil.
Lard.	Resin oil.
Lard oil.	Pine resins.
Butter.	Turpentine.
Bees'-wax.	Japan wax.

In this division must be included glycerin and the fatty acids of the first division; hence the blown oils give an increased weight of soluble product proportional to the loss of glycerin; this fact will explain why an old oil will give less insoluble matter than one comparatively new. By treating a mixture with ozonised oxygen, an oil easily oxidised can be separated from one not so readily acted on. Sulphur chloride will convert one into an insoluble product, whilst the fatty acids of the other can be washed out with carbon disulphide.

When acting on these products with nitric acid, as in estimating sulphur, a few drops of nitro-glycerin are formed, which should be carefully removed in the course of the analysis.

The presence of glycerin in many oils of the second division makes it difficult to understand why they behave so differently to those of the first division. A prominent feature is that they yield smaller weights of total magma than those of the first division, and which is readily seen

when oils of the two divisions are mixed. I give here a few oils of the second division, including a heavy lubricating petroleum, where the action of sulphur chloride may be taken as nil. 5 grms. being used in each case:—

Name of oil, &c.	Magma. Total.	Remarks.
Petroleum	5'01	} Entirely soluble in carbon disulphide.
Cocoanut	5'14	
Lard oil	5'80	
Sperm	6'16	

Petroleum and the distillates from coal-tar act simply as solvents of sulphur chloride, and it is by no means improbable that some of the oils of the second division act to some extent in the same way, and so prevent the formation of a magma; for, in every case, even with the oils of the first division, the solvent must be evaporated before the reaction sets in.

A mixture of two oils, both either belonging to the first or second division, or one of each division, can be quantitatively determined by the Hubl reagent, using equations (1) and (2) given in CHEMICAL NEWS, vol. lxii., p. 179.

In cases where an oil contains a peculiar isolable principle, we may apply the fact as chemical evidence of its existence, and neglect the separation for purposes of estimation. But when three or four oils are mixed, the isolation of a principle peculiar to one enables us to eliminate that one. We must be careful in applying this too rigidly; cocoanut oil may contain the glycerides of capric and butyric acids, according to the uses to which this oil may be applied. These acids are now commercial products, and, presumably, are not to be regarded simply as chemical curiosities.

A NEW METHOD FOR THE VOLUMETRIC DETERMINATION OF MANGANESE.

By G. VORTMANN.

THE iodometric determination of manganese has hitherto been effected by converting it into peroxide by means of any oxidising agent, and titrating this by treatment with hydrochloric acid and potassium. Such methods are mostly circumstantial, requiring careful filtration; and sometimes distillation according to Bunsen's process. The author endeavoured to determine manganese by oxidising it with standard solution of iodine in presence of an alkali, and ascertaining the quantity of iodine necessary for converting the manganous oxide into manganese dioxide. In all the experiments where he used a pure manganese salt alone, the values found were too low. To one atom of manganese there were consumed not two two atoms of iodine, but only 1'84 to 1'86.

The addition of a zinc salt, as in Vortmann's process, made no difference. But if there was added to the manganese salt, the salt of a sesquioxide, aluminium, or iron, the oxidation went off smoothly; two atoms iodine being consumed for one atom of manganese. If it is required to determine manganese alone, in the absence of other methods, the following procedure is followed:—

The weighed quantity of the manganese salt is dissolved in water, along with two or three parts of potash-alum, the solution is mixed with a measured quantity of a decinormal solution of iodine and pure soda-lye (free from nitrite). The whole is then heated in the water-bath for five to ten minutes, and, when cold, it is diluted to a known volume. An aliquot part of this is filtered off through a dry folded filter, the filtrate is acidulated, and the excess of iodine is titrated with solution of sodium thio-sulphate; the c.c. of the latter consumed are re-calculated for the total volume of the liquid and deducted from the quantity of iodine solution employed. Thus we obtain

the quantity of solution of iodine which was required for oxidising the manganous oxide.

Manganese can be conveniently determined in this manner in presence of aluminium or iron salts, or in crude iron.

Salts of ammonium must not be present.—*Berichte der Deutschen Chem. Gesellschaft*, vol. xxiii., No. 13, p. 2801.

AN IMPROVED PROCESS FOR THE MANUFACTURE OF POTASSIUM CYANIDE.

By H. N. WARREN, Research Analyst.

THIS method for the production of potassium cyanide, which depends, in the first place, upon the formation of potassium sulphocyanate, and the conversion of that substance into potassium cyanate, and, lastly, that of potassium cyanide, is brought about as follows:—

A proportionate quantity of carbon disulphide is blended with an equal bulk of mineral oil, to which is added a convenient quantity of water. Ammonia gas is now introduced until the whole of the CS_2 is converted into ammonium sulphocarbonate. The concentrated solution thus formed is separated from the remaining oil, and a fresh quantity of CS_2 added, the action proceeding as before. The solution containing the ammonium sulphocarbonate is now allowed to boil until all traces of ammonium sulphide have been expelled, the ammonium sulphocarbonate becoming converted into ammonium sulphocyanate. To the solution, while still hot, is introduced a sufficiency of KHO, and the heat maintained while any NH_3 gas continued to be evolved, the gas thus expelled being utilised for the production of a further quantity of ammonium sulphocarbonate; the resulting solution of KCNS thus formed is evaporated to dryness, and introduced into a deep crucible, being subjected to a dull red heat in contact with litharge; the KCNS thus being converted into potassium cyanate, with the production of PbS. The crucible with its contents is then allowed to settle, and the melt removed by decanting into a further pot, furnished with a perforated lid and containing lump carbon, the heat is now raised and continued at full redness as long as any traces of CO_2 or CO continue to escape. The resulting KCN thus obtained is poured from the pot and received into suitable moulds.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

THE DETECTION OF IODINE.

By W. H. SEAMON.

THE reaction of potassium iodide with the platonic salts, mentioned in Watts's "Dictionary of Chemistry," vol. iii., p. 288, furnishes a valuable test for the soluble iodides, being characteristic and delicate. The manner of making the test is as follows:—

To the solution in a test-tube add one or two drops of solution of platonic chloride. As the platonic chloride mixes with the liquid, a beautiful red colouration is produced, due to formation of platonic iodide. If much iodide be present the solution becomes black with subsidence of a brownish precipitate.

Free potassa, ammonia, and hydrochloric acid require the addition of a large amount of the platonic chloride. It is therefore best to have it neutral or acid with sulphuric acid. The reaction is plainly visible if $\frac{1}{1000}$ part of iodine be present, and is readily seen, though faint, with $\frac{1}{100}$ part of iodine.

The test has been subjected to a large number of trials to prove its value with most satisfactory results.—*Journal Analytical Chemistry*, Vol. iii., Part 3.

A RE-DETERMINATION OF THE ATOMIC WEIGHT OF CADMIUM.

By EDWARD A. PARTRIDGE, MA., B.S.

THE atomic weight of cadmium had been determined by Stromeyer, Von Hauer,* Lenssen,† Dumas,‡ and Huntingdon.§ With O=16 for the basis of calculation the values obtained by these experimenters are the following: by Stromeyer 111.48, by Von Hauer 111.96, by Lenssen 112.08, by Dumas 112.25, by Huntingdon 112.24. From these results Clarke calculates 112.092 to be the most probable figure, and concludes his article on the subject with this remark: "It will be seen that Dumas's and Huntingdon's determinations both made with haloid salts of cadmium agree with wonderful closeness and so confirm each other. On the other hand, Von Hauer's data give a value which is much lower. Apparently Von Hauer's method was good, and the reason for the discrepancy remains to be discovered. Until that is ascertained, I prefer to use the above mean value rather than to adopt one investigation and reject the others."

This investigation was undertaken with the hope of arriving at a value for the atomic weight of cadmium more reliable than that given by former experimenters.

The following points were regarded as of first importance:—

1st. The most scrupulous care in the purification of the materials used in every stage of the work.

2nd. Avoidance of any method in which the reactions involved were uncertain or doubtful.

3rd. The utmost care and refinement in weighing.

4th. Use of a large number of determinations as the basis of calculation.

At the outset much time was devoted to making a pure cadmium salt by re-crystallisation of the sulphate, and much work was devoted to accumulating a stock of this as the starting point. This, however, was discarded in favour of the metal obtained by distillation.

The literature upon this subject is interesting, though somewhat meagre. Mercury has been purified by distillation for years. Demarcay|| in 1882 observed that zinc and cadmium are volatile in vacuo at comparatively low temperature, and suggests this as a means of purification. In 1884, Schuller¶ stated that zinc and cadmium can be distilled in vacuo, leaving the impurities as a residue. This method has been employed by Morse and Burton** for the purification of zinc. One of the means employed by Stas in his classical investigation upon atomic weights was the purification of silver by distillation. Whenever available, distillation ranks first among the processes for purification at the disposal of the chemist. This was effected in the case of cadmium in tube retorts of glass, about 30 c.m. in length, and 20–25 m.m. in diameter.

The tubes were closed at one end and drawn down at a point about 11 c.m. from the closed end, making a neck about 12 m.m. in diameter. 100 grms. of cadmium having been introduced, the open end was drawn down to a size suitable for a connection with the mercury pump. The portion of the tube between the neck and the end connected with the pump serves to condense and retain the distilled metal.

After having been supported on a combustion furnace, the retort was exhausted as completely as a rapidly acting three-fall mercury pump would effect in one hour; the gauge then standing only a fraction of a m.m. lower than the barometer. As the pump was self-acting this degree of exhaustion was readily maintained during the entire

* *Jour. für Prakt. Chemie*, xxii., 350.

† *Ibid.*, lxxix., 281.

‡ *Ann. Chem. Pharm.*, lxi., 27.

§ *Proc. Amer. Acad.*, 1881.

¶ *Comptes Rendus*, xcv., 183.

** *Ann. d. Phys.*, xviii., 320, and *Jahresbericht*, 1884, 1550.

*** *Amer. Chem. Jour.*, x., 311.

operation. Heat was then slowly applied and so managed that the greater part of the metal condensed and ran down the sides of the retort, only the more volatile portion passing beyond the neck of the tube. A fractional distillation was thus effected, cadmium alone passing over. In an hour 60 grms. of cadmium had collected in the receiver, the distillation was then stopped, and when entirely cold the metal was removed by cutting open the tube. The greater part of it collected as a bar at the bottom of the receiver, while the sides and top were lined with crystals, many of which were quite perfect. The residue in the retort was covered with a brownish black scum, which was tested spectroscopically and found to consist mainly of lead, iron, and thallium, with a little copper. The lines of zinc were once very faintly seen.

The cadmium thus purified was distilled a second time in the same manner. The residue from this distillation, which was pushed no further than the first, remained perfectly bright to the end, and when tested with the spectroscope did not reveal a trace of foreign metals. All the cadmium used in this investigation was thus purified by double distillation.

One of the methods used for the determination of the atomic weight of cadmium is that of Lenssen, which, although good, was merely touched upon by him. His result was based upon only three experiments, using very small quantities of material. The method consists in changing cadmium oxalate to cadmium oxide, and observing the loss of weight, from which loss the atomic weight is calculated.

For working this method cadmium oxalate was made as follows:—

The perfectly pure metallic cadmium obtained by double distillation was dissolved in pure nitric acid, prepared by careful distillation, and the solution concentrated so far that on cooling the cadmium nitrate, $\text{Cd}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$, separated in long fibrous crystals. The latter were drained at the filter-pump, dissolved in water, and a solution of the theoretical amount of pure oxalic acid added. Cadmium oxalate thus prepared is a heavy crystalline precipitate which can be easily washed. This was done several times by decantation. The precipitate was then placed on a filter and washed at the pump thirty times with distilled water, after which it was dried for 20 hours at 150°C . The salt thus obtained was tested for nitric acid by the phenol test, and showed not the slightest trace. The pure cadmium oxalate thus obtained was subjected to the following treatment:—

About one gram. of cadmium oxalate was placed in a porcelain crucible and was then dried in an air-bath at 150°C . for five hours. This length of time was usually sufficient to dry the salt completely. When this had been accomplished, i.e., when a constant weight had been attained, the crucible containing the oxalate was covered with a watch-glass, and very cautiously heated. This operation required the greatest care, since if the temperature became too high, reduction and consequent volatilisation of metal occurred. Four of the earlier experiments were lost in this way. That volatilisation of metal had taken place was made evident by a slight sublimate on the watch-glass. When the oxalate was completely decomposed (this was shown by the uniform brown colour of the resulting cadmium oxide) it was allowed to cool and moistened with a few drops of nitric acid in order to re-oxidise any reduced metal. The nitric acid employed for this purpose was especially purified by very careful distillation. Ten c.c. of it evaporated in a platinum dish left a visible but imponderable residue.

The crucible was then very carefully ignited until all the cadmium nitrate was decomposed, then placed inside a nickel crucible 4 c.m. high by 4 c.m. wide, and strongly ignited for half an hour by means of a Fletcher's improved Bunsen burner. In all cases the ignition was repeated until a constant weight was obtained. There was rarely, however, any loss of weight after the first ignition. To prevent the possibility of any reducing gases reaching the

cadmium oxide, the nickel crucible inside which the porcelain crucible was placed was forced into a circular hole cut in a piece of asbestos board 13 c.m. square. The top of the nickel crucible was flush with the upper surface of the board, the joint being air-tight.

Ten experiments made by the above method gave the following results:—

Series I.

	Weight of cadmium oxalate taken.	Weight of cadmium oxide found.	Atomic weight.
1	1.09898	0.70299	111.819
2	1.21548	0.77746	111.793
3	1.10711	0.70807	111.755
4	1.17948	0.75440	111.780
5	1.16066	0.74237	111.783
6	1.17995	0.75471	111.784
7	1.34227	0.85864	111.829
8	1.43154	0.91573	111.823
9	1.53510	0.98197	111.821
10	1.41311	0.90397	111.834
Total..	12.66368	8.10027	(111.8027)
Mean value			111.8027
Maximum			111.834
Minimum			111.759
Difference			0.075
Probable error			0.010

Another method used for the determination of the atomic weight of cadmium is that of Von Hauer. It consists in reducing cadmium sulphate to cadmium sulphide in a stream of hydrogen sulphide and observing the loss of weight. As the result obtained by Von Hauer is considerably lower than those obtained by other experimenters doubt has been cast upon its accuracy. The following possibilities have been suggested as tending to make Von Hauer's results low:—(1) That the cadmium sulphate as weighed by him contained hygroscopic moisture. (2) That the presence of metallic iron in the ferrous sulphide used in making the hydrogen sulphide would lead to the generation of hydrogen and consequent reduction and volatilisation of cadmium. (3) That some cadmium sulphide might have been volatilised in the stream of hot hydrogen sulphide.

It was, therefore, determined to carry out a series of experiments by this method in order to determine if any of these objections were well grounded.

In the experiments about to be described, the first danger was overcome by weighing the sulphate in stoppered glass tubes. The second was shown to be groundless, as in some experiments the hydrogen sulphide used was prepared from antimony trisulphide, and in others from ferrous sulphide with perfect agreement of results. The third objection was disproved experimentally, as the highest heat that hard Bohemian glass will withstand did not cause any volatilisation of cadmium sulphide. That there was no volatilisation of sulphide was proved by the weight of a sample of the same which was heated in a stream of hydrogen sulphide to the extent just mentioned, remaining absolutely constant, and also by the fact that there was not the slightest sublimate on the tube.

The hydrogen sulphide employed in this and in the following series of experiments was washed by passing it through water and dried by passing through a long calcium chloride tube. The carbon dioxide was dried by passing through a wash bottle containing sulphuric acid, and then over calcium chloride. By means of a three-way cock the carbon dioxide could be run into the apparatus without changing the connections.

The cadmium sulphate was prepared in the following manner:—Cadmium nitrate, prepared as above described, was dissolved in water and a slight excess of pure sulphuric acid added. Five c.c. of this acid were evaporated in a platinum dish, leaving a visible but imponderable residue.

The solution was evaporated to dryness in a platinum dish and heated long after fumes of sulphuric acid ceased to come off. The sulphate was dissolved in water, recrystallised, and dried for six hours at 200° C.

The following is a description in detail of the method used in the experiments, the results of which are tabulated below. (Series II.)

The dry cadmium sulphate was placed in a porcelain boat and heated for some time in an air-bath to about 300° C. While still warm, the boat was placed in the weighing tube, allowed to cool, and weighed. Cadmium sulphate parts with its hygroscopic moisture very readily at 300° C. After weighing, the boat containing the cadmium sulphate was placed in a hard glass tube, 50 c.m. in length, supported over a small combustion furnace. A stream of pure dry hydrogen sulphide was then passed through the tube, and heat applied. It was heated moderately for 45 minutes, and to dull redness for as much longer. By this time its reduction to sulphide was always complete. It was then allowed to cool to about 200° C. in a slow stream of gas. When the temperature had fallen to this degree the hydrogen sulphide was displaced by a stream of pure dry carbon dioxide, and while still warm the boat containing the cadmium sulphide was placed in the weighing tube, allowed to cool, and weighed. Ten experiments by this method gave the following results:—

Series II.

	Weight of cadmium sulphate taken.	Weight of cadmium sulphide found.	Atomic weight.
1	1.60514	1.11076	111.793
2	1.55831	1.07834	111.789
3	1.67190	1.15669	111.790
4	1.66976	1.15554	111.818
5	1.40821	0.97450	111.801
6	1.56290	1.08156	111.806
7	1.63278	1.12985	111.778
8	1.58270	1.09524	111.797
9	1.53873	1.06481	111.796
10	1.70462	1.17962	111.801
Total	15.93505	11.62717	(111.7969)
Mean value			111.7969
Maximum			111.818
Minimum			111.778
Difference			0.040
Probable error			0.008

In the course of the work the experiment of passing hydrogen sulphide over gently heated cadmium oxalate was tried. This salt was completely transformed into the sulphide at a temperature much below that which is necessary for its conversion into cadmium oxide. This reaction was then made the basis of a new method for the determination of the atomic weight of cadmium. The method used in the ten experiments, the results of which are given below (Series III.), was as follows:—

Cadmium oxalate was placed in a porcelain boat and dried at 150° C. to a constant weight. It loses all of its moisture at that temperature. While warm the boat was placed in the weighing tube, allowed to cool, and weighed. The boat containing the cadmium oxalate was then placed in a tube arranged for passing hydrogen sulphide and supported over a combustion furnace as above described. The reducing gas was passed through the tube and heat slowly applied. When the contents of the boat had been completely changed to sulphide, the heat was raised to incipient redness, and kept at that temperature for about one hour. The cadmium sulphide was allowed to cool to about 200° C. in a slow stream of hydrogen sulphide, which was then displaced by a stream of pure dry carbon dioxide. While still warm the boat containing the cadmium sulphide was placed in the weighing tube, allowed to cool, and weighed. In every

case the sulphide was re-heated in the stream of hydrogen sulphide. There was never any volatilisation of cadmium sulphide, as the weight always remained the same, although in some experiments the sulphide was heated three times as long as in others. Moreover, there was never any sign of volatilisation either on the boat or on the tube. Ten experiments by the above method gave the following results:—

Series III.

	Weight of cadmium oxalate taken.	Weight of cadmium sulphide found.	Atomic weight.
1	1.57092	1.13065	111.812
2	1.73654	1.24979	111.786
3	2.19276	1.57825	111.824
4	1.24337	0.89492	111.823
5	1.18743	0.85463	111.807
6	1.54038	1.10858	111.771
7	1.38905	0.99974	111.806
8	2.03562	1.45617	111.833
9	2.03781	1.46658	111.774
10	1.91840	1.38075	111.814
Total	16.85228	12.12906	(111.8050)
Mean value			111.805
Maximum			111.833
Minimum			111.771
Difference			0.062
Probable error			0.009

The mean of the three series gives 111.8015 as the atomic weight of cadmium, with $O=16$.

The following is a description of the methods and apparatus used in the weighings:—In the experiments by Lessen's method two crucibles were used, one as a counterpoise. This dummy was treated in every respect in the same manner as the crucible containing the material operated upon. For weighing the crucibles, small beakers, with glass covers ground on, were provided. These beakers were adjusted so that their weights were approximately equal. The balance being provided with two riders, one of them was used to obtain adjustment with the beakers on the pans, while the other was used in the actual weighing after the crucibles were introduced. The beakers were never touched with the hands, but were taken in and out of the balance case by means of tongs, and the crucibles were introduced into the beakers with platinum forceps. The adjustment of the balance with the beakers on the pans was tested before and after every weighing, and during the entire series of experiments the greatest variation was 0.0001 grm.

For weighing the boats used in the second and third series of experiments, light glass tubes, with accurately fitting stoppers of glass, were made. Two boats were used in every experiment, one as a counterpoise. The boats, while still warm, were placed in the tubes and the tubes stoppered. When quite cold the stoppers were momentarily loosened to restore the atmospheric equilibrium inside the tubes.

The balance used was most accurate and highly sensitive, of the short arm pattern, with an aluminium beam. With a load of 30 grms. in each pan the resting point was displaced two whole divisions by 0.0001 grm. The weights were adjusted with the utmost care, especially for this work. The weighings in all experiments were reduced to the vacuum standard.—*American Journal of Science*, Vol. xl., No. 239.

Determination of Carbon Dioxide by Difference of Weight.—H. Bornträger.—The author recommends the use of nitric acid for the expulsion of the gas in preference to hydrochloric. Any nitrogen compounds formed are absorbed in the state of nitrose by the sulphuric acid used for drying the gas.—*Zeit. f. Analyt. Chem.*, xxix., 2.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 6th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Gustavus Anthony Abrines, Waterport Street, Gibraltar; William Baxter, Fordingbridge, Hants; T. St. John Belbin, Bolton Mansions Hotel, Scuth Kensington; John Thomas Brierley, 249, Bolton Road, Chorley, Lancashire; William J. Butcher, Emanuel College, Wandsworth Common; William Waters Butler, Elmdon, Selby Park, near Birmingham; Frank Brownsword, Heaton Moor, Stockport; M. Kelway Bamber, The Lodge, St. Waltham, Chelmsford; Ernest Bentz, 147, Bishop Street, Alexandra Park, Manchester; Arthur E. Barrows, Bloomfield Iron Works, Tipton, Staffordshire; W. E. B. Blenkinsop, 15, Earlsford Road, Wandsworth Common; Thomas Arthur Cheetham, 29, Park Road, Glasgow; Arthur William Crosskey, Bentcliffe, Accrington; Arthur William Cooke, 15, Belle Vue Terrace, Leeds; Frederick Hudson Cox, 79, Angell Road, Brixton, S.W.; William L. Dudley, Nashville, Tennessee, U.S.A.; Thomas Edwards, Brewery House, Rhymney, Monmouthshire; Walter N. Edwards, 4, Herne Hill Road, S.E.; Thomas S. Goodwin, Montgomery Cottage, Newton, Glasgow; Alfred Henry Green, Oaklands, Lowton, Newton-le-Willows; William Mahowe Heller, St. Dunstan's College, Catford, S.E.; John C. Hewlett, Elm-hurst, Beckenham, Kent; Charles Terry Holloway, Apsley Villa, Lewisham High Road, S.E.; John Richard Jackson, 51, Abbotsof Place, Glasgow; John Jackson, Tredegar Road, Rhymney; Joseph Lunt, 5, South View, Eccleston Road, Ealing, W.; George Griffiths Leason, Ashfield Cottage, Stoke-on-Trent; Harry C. Myers, Strassburg, Germany; William Mackeay, 2, Victoria Mansions, S.W.; Thomas Smith Murray, 7, Gayfield Square, Edinburgh; William Reginald Ormandy, Park Road, Newton-le-Willows; James Alexander Pond, Auckland, New Zealand; Thomas Platts, 7, Victoria Street, London; Henry Ramsen Redman, 10, The Gardens, Dulwich, S.E.; G. H. Robertson, 30, Hemstall Road, West Hampstead, N.W.; Charles William Seacombe, Church Park, Witchurch, Tavistock; Ernest Henry Sainter, 176, High Street, Redcar; J. Napier Spence, 9, Headstone Terrace, Harrow; Thomas Steel, Jarraville, Melbourne, Victoria; John Joseph Sudborough, 111, Stratford Road, Birmingham; Charles Thomas Sprayne, Reinsgraben, Göttingen; Francis Henry Tate, 9, Hackins Hey, Liverpool; John Cundall Wood, 32, Frederick Street, Sunderland; George Henry Wadsworth, 3, Southfield Square, Lamb Lane, Bradford; Sidney Wood, 5, Woodview, Bradford, Yorks; George Young, 5, Colinton Road, Edinburgh.

The following papers were read:—

83. "The Magnetic Rotation of Saline Solutions." By W. H. PERKIN, Ph.D., F.R.S.

On account of the remarkable results given by solutions of the halohydrides and their compounds with ammonia and organic bases when examined as to their magnetic rotatory power (*cf. Chem. Soc. Trans.*, 1889, 740), it became important to study the solutions of metallic salts in a similar manner, and although the work which has been done in this direction is incomplete, and may occupy some time yet, the results, as far as they go, are of interest, especially in relation to the question of the condition of substances in solution. The substances which have been examined up to the present are chiefly chlorides, bromides, iodides, nitrates, a nitrite, sulphates, and phosphates, also hydroxides of the alkali metals.

In the following comparisons, the values taken for the halogens are those found for them in their compounds

with the alcohol radicles, *i.e.*, Cl = 1.733, Br = 3.562, I = 7.757. Those for the metals are deduced from the rotations of their nitrates, because in the case of ammonium nitrate, it was found that this salt gave a rotation which was practically normal, and the salts of the metals have been found to behave in a similar manner to those of ammonium. Should there be any errors in these calculated values of the metals they will be but small, and therefore will not materially influence the character of any deductions that may be made from the rotation of their compounds. They are Na = 0.558, K = 0.809, Li = 0.398, Ca = 0.691, Mg = 0.577.

The solutions examined were for the most part either saturated or supersaturated; in the case of sodium iodide, lithium nitrate, and sodium hydroxide, two strengths, varying considerably from each other, were taken, but the results were found to be practically the same. In the case of lithium chloride, which forms much stronger solutions than any of the other chlorides, bromides, or iodides examined, the rotation increased on dilution, as in the case of hydrogen chloride.

LiCl + 3.213 mol. OH ₂	gave 4.166 mol. rot.
" + 7.411 "	" 4.559 "
" + 11.760 "	" 4.697 "

At present, this is the only salt known the rotatory power of which changes with the amount of water used, and probably, like hydrogen chloride, it will be found to give a stationary value before the above dilution of 11.760 mols. of water is reached; but further experiments must be made to establish the facts of the case.

In two instances, the effect of varying temperature was tried. A solution of sodium bromide was examined at 16° and 78.5°; in this case there was a small reduction in the molecular rotation at the higher temperature of 0.105; with a solution of potassium iodide, examined at 16° and 84.4°, there was also a small diminution at the higher temperature, but only of 0.024. Substances, especially if they have high rotations, give a slightly lower rotation at higher temperatures, like the above, than at lower temperatures: so that, allowing for errors of observation, these results indicate that practically little or no change in the nature of the solutions took place when they passed from one temperature to another.

The following tables show the calculated and found rotations of the substances examined and their relation-ship to each other:—

Haloid Compounds.			
	Calculated.	Found.	Ratio.
NaCl	2.291	5.068	1 : 2.212
KCl	2.542	5.377	1 : 2.115
LiCl	2.131	4.697	1 : 2.204
CaCl ₂	4.157	9.085	1 : 2.185
MgCl ₂	4.043	9.103	1 : 2.252
NaBr	4.110	9.030	1 : 2.197
KBr	4.371	9.222	1 : 2.110
NaI	8.315	18.867	1 : 2.269
KI	8.566	18.690	1 : 2.182

It will be seen that the rotations of these salts, when in aqueous solution, are practically 2.2 times greater than the calculated values for the dry substance; they are even greater than those of the analogous ammonium compounds, the calculated values for which now given differ by 1 from those previously published, which were to this extent incorrect.

	Calculated.	Found.	Ratio.
NH ₄ Cl	3.305	6.906	1 : 2.084
NH ₄ Br	5.134	10.196	1 : 1.985
NH ₄ I	9.329	19.996	1 : 2.144

A solution containing equi-molecular proportions of NaI and NaOH gave a rotation for NaI = 18.454, or 0.413 lower than that given by the iodide alone.

Hydroxides of Alkali Metals.

	Calculated.	Found.	Ratio.
NaOH	1'006	2'433	1 : 2'418
KOH	1'257	2'658	1 : 2'114

Here, again, a remarkable increase of rotation is obtained, quite as great, or even larger in one case, than with the halogen salts.

Potassium hydroxide in alcoholic solution gives a somewhat lower number than the above for its aqueous solution; but it is possible that some of the potassium in this instance may be in combination as alcoholate, and this may account for the difference.

Sulphates.

	Calculated.	Found.	Difference.
NaHSO ₄	2'419	2'525	0'106
Na ₂ SO ₄	2'513	2'877	0'364
Li ₂ SO ₄	2'099	2'379	0'280

In this table the difference is given instead of the ratio, and it will be seen that it is but small compared with the foregoing, but it increases with the number of atoms of metal.

Phosphates.

	Calculated.	Found.	Difference.
NaH ₂ PO ₄	3'328	3'481	0'153
Na ₂ HPO ₄	3'678	4'076	0'398
Na ₃ PO ₄	4'036	5'079	1'043

As in the case of the sulphates, the rotation increases beyond the calculated with the number of atoms of metal; in the last case the difference is considerable.

Potassium Nitrite.—This salt is interesting, because it allows of a comparison being made between it and potassium nitrate, which can be placed side by side with a similar comparison between isobutyl nitrite and nitrate.

	Difference.
KNO ₂	1'943
KNO ₃	1'535
C ₄ H ₉ NO ₂	5'510
C ₄ H ₉ NO ₃	5'180

From this it is seen that in both cases the nitrites give larger rotations than the nitrates, and the differences do not vary very greatly, though sufficient to show that the rotation of potassium nitrate undergoes some change when that salt is in solution.

Nitrates.

NaNO ₃	1'284
KNO ₃	1'535
LiNO ₃	1'124
Ca(NO ₃) ₂	2'143
Mg(NO ₃) ₂	2'029

It has been assumed that the solutions of the nitrates give practically normal results, and the values of the metals have been deduced from them: the reasons for this have already been given; it may be added that of all the salts examined the nitrates give the lowest numbers for the metals. Nevertheless, experiments are in progress to test the validity of this method of determining the values of the metals.

In considering the numbers given in this communication, it is well to remember that, owing to the method employed in calculating the results obtained from solutions, all experimental errors fall upon the numbers obtained for the dissolved substance, and consequently will also influence the differences found in comparing the results, as in the tables given above. When the solutions contain large percentages of dissolved substance, the errors are but small, but when the percentages are small the errors naturally increase; on this account it will be difficult to get good results with compounds that are sparingly soluble in water.

It is very difficult to understand why the haloid acids, their metallic derivatives and also caustic alkalis should give such extremely large rotations when in aqueous solution. If dissociation takes place there does not seem to be any reason why any very considerable change of rotation should occur, but whatever the cause, the change evidently indicates some very important difference existing between dissolved and undissolved substances of these classes.

DISCUSSION.

Dr. GLADSTONE remarked that similar excessive values were obtained on determining the refractive powers of solutions of metallic chlorides, &c., although the difference between the calculated and observed values were much smaller than in the case of Dr. Perkin's measurements. It was all-important to determine the difference in the behaviour to light of a substance in its solid state and when in solution, but this was difficult as few solids were uniaxial; as an example of the difference he mentioned that in the case of sodium chloride the solid has a refraction of 14'4, while that of the dissolved substance is 15'3.

Mr. PICKERING said that Dr. Perkin's results must have a very important bearing on the question of the nature of solutions. When salts caused a double depression of the freezing point, the physicists held it to be due to dissociation into ions; but here was a case of a similar effect which cannot well be attributed to dissociation. As far as can be seen, dissociation would not double the rotation, still less would it make it more than double, and even if it could be held to do so, such an explanation would be inadmissible in the case of saturated solutions, for in such solutions the physicists themselves held that there is little or no dissociation.

Professor RAMSAY thought that the abnormal results may not be entirely connected with dissociation into ions, the optical phenomena were probably much more complex; it was conceivable that the separated atoms might be much more powerfully affected in a magnetic field than when combined.

84. "Note on Normal and Isopropylparatoluidine."—By E. HORI and H. F. MORLEY.

Desiring to distinguish with certainty between normal and isopropylparatoluidine, the authors have prepared the pure substances and several of their derivatives.

The normal compound boils at 230-233°; its density at 20° is 0'9243 grm. per c.c., and at the boiling point 0'7543; hence its molecular specific volume is 197'53 (theory 199'5); its molecular refractive energy is 82'5 (theory 79'3).

Isopropylparatoluidine boils at 219-221 (uncorr.); its density at 20° is 0'9226 grms. per c.c., and at the boiling point 0'7466; hence its molecular specific volume is 199'57; its molecular refractive energy is 81'4.

The isopropylnitrosamine is a crystalline solid, whereas the isomeride is an oil.

The normal and iso-compound form oxalates differing in solubility and stability.

85. "The Action of Light on Ether in Presence of Oxygen and Water." By ARTHUR RICHARDSON.

In a recent paper by Professor Dunstan and Mr. Dymond (*Chem. Soc. Trans.*, 1890, 574), it is stated that hydrogen peroxide is not formed when pure ether is exposed to light in contact with air and water, and these authors consider that the formation of this substance is due to the impurities contained in the ether, which can be removed by treatment with potassium bichromate or iodhydric acid. The author describes experiments made with ether which had been purified by some of the methods described by Dunstan and Dymond; he finds that hydrogen peroxide is formed in the liquid in every case after exposure to light in contact with moist air or oxygen, but not in the dark at the ordinary temperature. The methods employed to prepare and purify the ether are described in full in the paper; they were as follows:—

1. Commercial "pure" ether, from which the alcohol had been removed by repeated shaking with water, was afterwards agitated with potassium bichromate.

2. Ether obtained by the action of pure sulphuric acid on pure alcohol was shaken with potash solution and with water, and one portion was treated with potassium bichromate, another with iodhydric acid.

3. The liquid from 2 was collected after exposure to light, and again agitated with potassium bichromate.

4. Ether prepared from an entirely different sample of pure alcohol and pure sulphuric acid was treated as before with potassium bichromate; it was distilled after being allowed to stand over calcium chloride and then over metallic sodium. The ether boiled constantly at 34.6° at 760 m.m. pressure corr. to 0° .

The ether prepared by these methods was placed in colourless bottles, and air or oxygen was passed into the space above the liquid before the stoppers were inserted.

Some experiments were made on the influence of temperature in bringing about the formation of hydrogen peroxide; it was found that ether and moist oxygen exposed to a temperature of $75-88^{\circ}$ in the dark contained, after four days, considerable quantities of this substance; similar results were obtained when ether and oxygen were heated to 60° for a period of forty hours. Ether vapour and moist oxygen gave practically no peroxide when so heated. It was found, however, that liquid ether kept at 0° contained hydrogen peroxide after exposure to light for four days.

Hence, it appears that when special precautions are taken to ensure the presence of oxygen over the ether, hydrogen peroxide is formed at ordinary temperatures, and even at 0° in the light, but not in the dark; it is, however, formed in absence of light at about 60° .

DISCUSSION.

Professor DUNSTAN said that Mr. Dymond and he had made their experiments on the conditions necessary for the formation of hydrogen peroxide from ether, because there was no evidence that previous workers had employed the pure substance. They had been unable to detect hydrogen peroxide in ether that had been exposed at a low temperature to the electric light and diffused daylight. For the detection of hydrogen peroxide, reliance had been placed on the characteristic chromic reaction which they had proved to be capable of indicating 0.0002 grm. of the substance. Dr. Richardson, who meanwhile had purified ether by the method employed by the speaker, and still adhered to some of his original statements, asserted that he had detected hydrogen peroxide in ether exposed at a low temperature to white light by means of titanium oxide, but it appeared that he had failed to obtain the chromic reaction. The suggestions which Dr. Richardson had made to explain why hydrogen peroxide had not been formed in their experiments were quite untenable. At least 2 litres of air were in contact with the exposed ether. There could be no doubt as to the purity of the ether they had used. The slight greenish tint of the bottles was shown not to be detrimental by the circumstance that hydrogen peroxide was produced from specimens of impure ether contained in them. They had employed the electric light partly because they had failed to obtain results with diffused sunlight in London, and partly because they wished to ascertain whether pure ether was affected by violet rays acting at a low temperature. They had recently obtained evidence which seemed to show that certain specimens of unpurified ether could form hydrogen peroxide even in the dark. The whole purport of Dr. Richardson's first paper on this subject was to prove that when hydrogen peroxide is formed from moist ether, the water and not the ether is oxidised. They had opposed this view as they were in possession of good evidence that the ether is oxidised. It now appeared that Dr. Richardson had abandoned his former view, although he still contended that hydrogen peroxide could be formed from water and oxygen alone in the presence of light.

But they had also failed to confirm this statement. No evidence could be obtained of the presence of hydrogen peroxide in acidulated water which had been exposed to intense sunlight or to the electric light (*cf. Chem. Soc. Trans.*, 1890, 988). They were also unable to confirm the statement that pure ether yields hydrogen peroxide when heated with air and water to $50-60^{\circ}$.

Mr. DYMOND said that Dr. Richardson had not stated whether he had tested his ether for the impurities which are known to be invariably present, some of which may be produced during the process of purification employed, and which are particularly difficult to remove, viz., aldehyd and ethylene. In his previous paper, Dr. Richardson had stated that after hydrogen peroxide had been produced in ether, the ether remained unaltered. Did he adhere to that statement now that he had convinced himself that the ether was concerned in the production of the peroxide? In the experiments made by Professor Dunstan and himself, it was always noticed that when peroxide of hydrogen was produced from ether, the ether afterwards contained aldehyd, acetic acid, and other substances.

Mr. GROVES, referring to Dr. Richardson's statement that he had found that pure dry ether was acted on when exposed with oxygen, said that this result was contrary to recent experience as to the influence of water in promoting chemical change; it was difficult to conceive how hydrogen peroxide could be produced in such a case.

Mr. PICKERING inquired why so minute an amount of peroxide was obtained; if pure ether afforded hydrogen peroxide when oxidised, it was to be expected that the action would continue, and that a larger proportion would result.

Dr. PERKIN said that the alcohol was best removed from ether by means of phosphoric anhydride. Dr. JAPP mentioned that Professor Frankland had always used this substance in purifying the ether used in preparing zinc methide; and Professors RAMSAY and DUNSTAN subsequently stated that they had employed it with good results.

Dr. RICHARDSON, in reply, stated that he did not see that Professor Dunstan's ether had any claim to greater purity than that used by himself. On the contrary, the fact that Professor Dunstan's ether distilled only within $\frac{1}{2}$ degree showed that it was not so pure as that used by him, which distilled within 1-10th degree. The ether used by the speaker was found to be without action on potassium iodide in the dark after contact with the solution for two weeks. With regard to the remarks made on the quality of the bottles used, it appeared to him that the fact that methylated ether was found to contain H_2O_2 after exposure to light in greenish glass bottles, did not show that the formation of this body was in this case brought about by light at all, for, as Professor Dunstan had just pointed out, impure ether which had been kept in the dark was found to contain this substance. He did not see that the absence of H_2O_2 in Dunstan's ether could be accounted for by the use of the electric light, for Professor Dunstan states (*Chem. Soc. Trans.*, 1890, 579) that in one series ether was exposed for two months to much sunlight during August and September, the temperature ranging between $15-25^{\circ}$, but, under these circumstances, no H_2O_2 was formed. The speaker would like to point out that in all except the last sample of ether he had obtained sufficient H_2O_2 after exposure to give the blue colouration with $K_2Cr_2O_7$; in the last case, however, the time of exposure had been necessarily short, and the light exceedingly poor, so that the presence of H_2O_2 could only be detected by the more delicate tests such as KI and H_2TiO_3 . He was not surprised to learn that Professor Dunstan had failed to obtain H_2O_2 on exposing H_2O to light, for in the formation of this body, under these conditions, many special precautions must be observed, such as keeping the temperature low, &c., as he found that the H_2O_2 first formed was very readily decomposed.

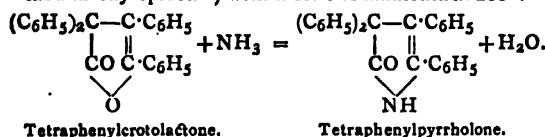
In reply to Professor Pickering, Dr. Richardson wished to point out that other products of decomposition were

formed when ether was exposed to light, some of which might probably decompose the peroxide first formed; thus a specimen of ether which had been exposed with water and oxygen to light for 18 months contained no H_2O_2 , the smell of the ether had changed, and black particles were seen floating in the liquid—this was a point which the author hoped to further investigate, however.

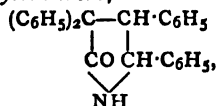
86. "Action of Ammonia and Methylamine on the Oxylepidens." By FELIX KLINGEMANN, Ph.D., and W. F. LAYCOCK, Ph.D.

This investigation was undertaken with the object of ascertaining whether the analogy which was shown by Japp and Klingemann to prevail between the interactions of $\alpha\beta$ -dibenzoylcinnamene and those of dibenzoylstilbene (Zinin's "acicular oxylepiden") was preserved in the behaviour of these compounds with ammonia and amines. The authors find that this is the case.

On heating dibenzoylstilbene with alcoholic ammonia at 200° , it is converted into a mixture of two isomeric compounds of the formula $C_{28}H_{21}NO$: *dibenzoylstilbenimide*, which is deposited from benzene in crusts of yellow prismatic crystals melting at 180 – 182° , and corresponds with bibenzoylcinnamenimide; and *tetraphenylpyrrholone*, which crystallises in pale yellow square plates melting at 206 – 207° , corresponding with triphenylpyrrholone. Dibenzoylstilbenimide is converted by heating at 310° into tetraphenylpyrrholone, just as dibenzoylcinnamenimide is converted into triphenylpyrrholone. The constitution of tetraphenylpyrrholone is shown by the fact that it is also obtained by heating tetraphenylcrotonolactone (Zinin's "tabular oxylepiden") with alcoholic ammonia at 200° :—

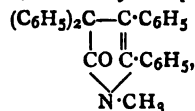


By the action of nascent hydrogen (from sodium and boiling amyl alcohol) tetraphenylpyrrholone is converted into *tetraphenylpyrrholidone*,—



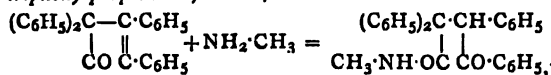
which crystallises from alcohol in slender pale brown needles melting at 237° .

When dibenzoylstilbene is heated with an alcoholic solution of methylamine at 200° , it is converted, with elimination of water, into *methyltetraphenylpyrrholone*,—



which crystallises from hot alcohol in thin faintly yellowish asymmetric plates melting at 161° .

On the other hand, tetraphenylcrotonolactone unites directly with methylamine at 150° , forming *benzoyltriphenylpropiomethylamide*,—



which crystallises from glacial acetic acid in lustrous plates melting at 267° . When this compound is distilled under reduced pressure, it parts with water and is converted into methyltetraphenylpyrrholone. The crystalline form of the compound thus obtained differed, however, from that of the same substance from dibenzoylstilbene, and the melting-point was found at 158° , instead of 161° ; but the authors attribute these differences to dimorphism, as in the case of the corresponding triphenyl derivatives prepared by Japp and Klingemann.

87. "Condensation of Acetone-phenanthroquinone." By G. H. WADSWORTH.

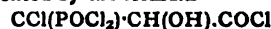
The author finds that by the dehydrating action of a mixture of concentrated sulphuric acid and absolute alcohol, acetone-phenanthraquinone is converted into a compound of the formula $C_{34}H_{22}O_3 = 2C_{17}H_{11}O_3 - 3H_2O$. It crystallises from benzene in tufts of minute needles melting at 238° C.

88. "Contributions to the Knowledge of Mucic Acid. Part IV. Action of Phosphorus Pentachloride on Mucic Acid." By S. RUHEMANN, Ph.D., M.A., and S. F. DUTTON, B.A., B.Sc.

The authors find that mucic acid is converted by the action of phosphorus pentachloride into a crystalline compound which, assuming dichloromuconic acid to be an acid of the formula—



may be represented by the formula—



On dissolving this substance in water and carefully concentrating the solution, large colourless rhombic crystals of the corresponding *phosphorodichloromuconic acid* are obtained; several salts of this acid are described, among others, one formed by the combination of $6NH_3$ with the acid. The phosphochloride is converted by the action of phosphorus pentachloride at 120° into dichloromuconyl chloride, hydrogen chloride, and phosphorus oxychloride.

The authors have succeeded in converting the isomeride of Bode's dichloromuconic acid discovered by Ruhemann and Elliot (*cf. Chem. Soc. Trans.*, 1890, 931) into Bode's acid, by adding a small quantity of bromine to the cold aqueous solution; they therefore conclude that the isomeric dichloromuconic acids are related to each other much as are maleic and fumaric acids.

89. "Halogens and the Asymmetrical Carbon Atom." By T. H. EASTFIELD.

At the suggestion of Professor Emil Fischer, the author has endeavoured to prepare active haloid derivatives similar in constitution to Le Bel's optically active secondary amyl iodide, $CH_3 \cdot CHI \cdot C_3H_7$, which at present stands alone as the only active compound in which a halogen is united to the asymmetric carbon atom. His results are negative. Thus active mandelic acid gave inactive phenylbromacetic acid when heated with bromhydric acid at a temperature not exceeding 50° ; and no resolution of the acid into active constituents was effected by means of alkaloid salts.

The following are the Titles of Papers received and printed in the *Transactions* during the recess :—

68. "Crystallographical Relations of the Derivatives of Dibenzoylcinnamene." By Alfred E. Tutton, Demonstrator in Chemistry at the Normal School of Science, South Kensington.

69. "Note on a Compound from Benzoin and Acetone." By Francis R. Japp, F.R.S., and Julius Raschen, Ph.D.

70. "Researches on Normal and Mixed Diazoamides." By Raphael Meldola, F.R.S., and F. W. Streatfield, F.I.C.

71. "Note on the Action of Nitric Acid on Dibromonaphthol." By Raphael Meldola, F.R.S., and Frank Hughes.

72. "A New Method for the Estimation of Nitrates and Nitrites in Water." By R. Ormandy and J. B. Cobes, Ph.D., Owens College, Manchester.

73. "A New Monobromocamphor." By J. E. Marsh.

74. "Contributions to the Knowledge of Mucic Acid. Part II. Action of Phosphorous Pentachloride on Mucic Acid." By S. Ruhemann, Ph.D., M.A., and W. J. Elliott, B.A.

75. "Contributions to the Knowledge of Mucic Acid. Part III. Hydromucic Acid." By S. Ruhemann, Ph.D., M.A.

76. "Note on the Reduction of Aromatic Amides." By A. Hutchinson, B.A., Scholar of Christ's College, Cambridge.

77. "Some Improved Vacuum Joints and Taps." By W. A. Shenstone.

78. "The Production of Camphor from Turpentine." By J. E. Marsh, B.A., and R. Stockdale, B.A.

79. "p-Desylphenol." By Francis R. Japp, F.R.S., and G. H. Wadsworth, Associate of the Normal School of Science.

80. "Paraxylenesulphonic Acids." By Gerald T. Moody, D.Sc., Demonstrator in the Chemical Department, City and Guilds of London Institute, Central Institution, and T. G. Nicholson.

81. "Action of Phosphoric Anhydride on Fatty Acids. Part II." By F. Stanley Kipping, Ph.D., D.Sc.

82. "An Investigation of the Conditions under which Hydrogen Peroxide is Formed from Ether. (Second Notice)." By W. R. Dunstan and T. S. Dymond.

PHYSICAL SOCIETY.

November 14, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

THE following communications were made:—

"On Certain Relations existing amongst the Refractive Indices of the Chemical Elements." By the Rev. T. PELHAM DALE, M.A.

The first part of the paper corroborates the results announced in a communication made in May, 1889, on the same subject, and says that, as far as experimental data are forthcoming, the refraction ($\mu - 1$), divided by the vapour density (d), is equal to a constant multiplied by some integer. Several metals whose refractions have since been determined conform to this law. On examining the relation between molecular weight (M) and refraction, similar conclusions are arrived at, for, to a fair degree of approximation, the ratio $M/\mu - 1$ is a constant or a simple multiple of this constant.

The question as to how far the relation $\mu - 1/d = c$ holds good for the same element in the three states of vapour, liquid, and solid, has been examined as far as data exist for this purpose. The resulting numbers are not identical, but some of the data themselves are doubtful.

Another relation is between the molecular distances (h) (see *Proc. Phys. Soc.*, vol. ix., p. 167), and the atomic weight (a) of the elements, h being nearly proportioned to $\sqrt{a}$. In the case of selenium, sulphur, and phosphorus, the agreement is close, but for bromine, chlorine, and carbon, not so good.

A fifth relation appears to exist between the upper limit of refraction and the line spectra of elements. For example, the upper limit of refraction for selenium occurs at wave length 5295.7, whilst its spectrum exhibits a remarkable series of strong lines about this wave length. A similar relation apparently holds with sulphur, phosphorus, and bromine. Gold also shows a series of strong lines about C, in the vicinity of which the metal has the greatest reflective power.

The author finds that selenium polarises and reflects nearly all the light that falls on it at a large angle, and suggests that it may be used in polariscopes.

He has also endeavoured to connect together the phenomena of a limit of refraction and anomalous dispersion. In the case of fuchsin the dark space coincides with the limit of refraction, and the same is probably true of cyanin. If one of the anomalous indices be given the other can be found. He also believes that bodies of high molecular weight give anomalous dispersion, and thinks solutions of iodine will exhibit the phenomenon.

The mathematical investigation of the whole subject involved difficulties arising from the want of reliable data, and the author hopes that some member will take up the necessary experimental determinations.

Dr. GLADSTONE thought the author under-estimated the amount of work done and in progress on the subject; for the question whether $\mu - 1/d$ is constant or not is being investigated by many. The French physicists, he said, had found the quantity nearly constant, but Lorenz's expression, $\mu^2 - 1/\mu^2 + 2$, is slightly better when applied to compounds in the liquid and gaseous states. Metals were difficult to deal with, especially as, according to the recent paper of Du Bois and Reubens, their refractions do not follow the law of sines.

Mr. DALE here suggested that they might be related to hyperbolic sines.

Dr. GLADSTONE, continuing, said that by taking solutions of metals, it was found that their specific refractive energies were nearly inversely as the square of their combining weights, but, at present, the known cases were not sufficient to establish a law.

Prof. RÜCKER said that of the two expressions, $\mu - 1/d$ and $\mu^2 - 1/\mu^2 + 2$, the latter seemed preferable, for it could be converted into electrical quantities by writing κ for μ^2 . The expression then became $\kappa - 1/\kappa + 2$, and if this can be shown to be constant by electrical work, this would be an argument in its favour.

On the subject of anomalous dispersion, he directed Mr. Dale's attention to Mr. Glazebrook's "Report on Optical Theory" made to the British Association.

Mr. DALE, in reply, pointed out that from the nature of the two formulæ, an inaccuracy or variation in μ would affect theirs more than Lorenz's. He thought that $\mu - 1/d$ was a limit towards which the numbers tend.

"Tables of Spherical Harmonics." With Examples of their Practical Use. By Prof. J. PERRY, F.R.S.

The author defined a Spherical Harmonic as a homogeneous function of x, y, z , satisfying the equation—

$$\frac{d^2V}{dx^2} + \frac{d^2V}{dy^2} + \frac{d^2V}{dz^2} = 0,$$

stated the fundamental properties of such functions, and pointed out their importance in problems on heat, electricity, and hydrodynamics. Referring to zonal harmonics (homogeneous functions of $(x^2 + y^2)^{\frac{1}{2}}$ and z), he showed that these harmonics are symmetrical with respect to the axis of z , and might be expressed as functions of the angle (θ) which the line joining the point (x, y, z) to the origin makes with the axis of z , multiplied by r^i ; where r is the radius vector, and i the degree of the homogeneous function. These functions of θ are called zonal surface harmonics, and are designated by P_0, P_1, P_2 , and P_i , according to the degree of the function. It was the values of these quantities which form the tables brought before the Society.

The tables comprise the values of P_1 to P_8 , and are calculated to four places of decimals, and for every 1° between 0° and 90° .

As an example of the use of such tables, the case of a spherical surface covered with attracting matter, whose density varied as the square of its distance from a diametrical plane, was taken. It was required to find the potential both outside and inside the sphere, and to determine the equipotential surfaces and lines of force. The potentials inside (A) and outside (B) were shown to be given by—

$$\frac{A}{\pi} = 8 + \frac{16}{5}r^2P_2 \text{ and } \frac{B}{\pi} = \frac{8}{r} + \frac{16}{5}\frac{1}{r^3}P_2$$

respectively. By giving A and B definite values, and choosing values of r , the corresponding P_2 's can be calculated, and the values of θ determined from the tables. Hence, any equipotential surface can be easily determined, and lines drawn to cut the surfaces orthogonally are lines of force.

Another problem which had been tried consisted in

finding the directions of the lines of force near a circular coil of rectangular cross-section, when an electric current circulates in the coil. This was treated approximately by first calculating the potential at six points along the axis in the neighbourhood of the coil, and then finding, by Gauss' method, the coefficients A_0, A_1, A_2 , &c., of an expression in ascending powers of s , which agreed with the calculated potentials at the points chosen. The formula $V = A_0 + A_1 r P_1 + A_2 r^2 P_2$, &c., or its corresponding expression in inverse powers of r , was then assumed to give the potential at any point in the space considered. By giving V definite values, a series of equipotential surfaces were determined, and the lines of force drawn. On putting the calculations to the test of experiment, the approximate solution of this very difficult problem was found to be very nearly correct.

NOTICES OF BOOKS.

Asbestos: its Properties, Occurrence, and Uses. With some Account of the Mines of Italy and Canada. By ROBERT H. JONES. London: Crosby Lockwood and Son.

THIS work took its origin in a pamphlet on the Canadian Asbestos Mines, and, as the author followed up the subject, it has expanded into an account of asbestos deposits throughout the world, and a summary of the industrial applications—actual or suggested—of this singular mineral.

It is a singular fact that, whilst the fire-proof character of asbestos was known and studied in antiquity, the material afterwards fell into disuse, and has only lately come again into notice.

Whilst fully accepting what Mr. Jones has to say on the many valuable attributes of asbestos, we cannot accept his statement that "occupying the position of a connecting link between the animal, vegetable, and mineral kingdoms, it possesses some of the characteristics of all three."

Concerning its fire-proof properties, he gives a hint which may prevent disappointments. Some varieties, we are told, have resisted a temperature of 5000° F., but the hydrous varieties lose their flexibility and become brittle at high temperatures.

The traditions handed down concerning the use of cloth woven from this fibre, and capable of being cleansed by throwing it into a charcoal fire, are sufficiently vague.

The possession of such a cloth is ascribed to Charlemagne, or, according to another version of the same story, to Charles V.

Marco Polo, about A.D. 1300 mentions the occurrence of this mineral in the region now known as Siberia, and gives a very accurate account of its extraction and preparation for use.

The economic importance of the Canadian deposits of asbestos does not seem to have been recognised prior to 1877. It is humiliating to find that in a work on the capabilities and productions of Canada which was got up by occasion of the "Colinderies," and intended for gratuitous distribution in the Dominion section, no mention was made of asbestos.

Asbestos, we are reminded, is not the name of any one particular mineral species, but is a generic term common to several minerals. They are all silicates of lime, magnesia, or alumina, varying much in density and colour, and most of them being flexible and elastic. *Asbestos proper*, which unfortunately does not occur in Canada, is a fibrous variety of hornblende. The Canadian mineral is a fibrous serpentine containing 12–14 per cent. of water.

Mountain wood, mountain cork, mountain leather, and mountain paper are sub-varieties in which the fibres instead of running parallel are matted and interlaced.

Various forms of asbestos occur in Australia and South Africa. The deposits in the United States are not of a quality and quantity to admit of successful working.

The author is of opinion that, though the chief supply of this mineral is from Italy and Canada, yet these countries will find Africa in the near future a formidable competitor.

The Italian mineral contains more magnesia and water than the Canadian and less alumina. It is less easy to work, and the product is less uniform.

It appears that the trick of "salting" mineral grounds intended for sale is not peculiar to the far side of the Atlantic. The Italian mine-owners drive fine asbestos fibre into the crevices of rocks, and give it, as far as possible, the appearance of the genuine formation.

Mr. Boyd, an authority here quoted, says that in Italy, "if asbestos is found on the surface of a rock exposed to the south or south-west, the product is generally fairly abundant, and of good quality."

If exposed to the east there is fine quality, but very small quantity; whilst if exposed to the north the quantity is plentiful, but dry and hard, and on entering the rock all traces of it are lost.

The Canadian asbestos, or chrysotile, has a very different character from the Italian. On its first appearance in the market it was met with contempt. Now, however, it is proved that mining for asbestos in Canada, if properly conducted, shows a more steady return for the money invested, with less elements of risk, than mining for any other material. The great difficulty to be encountered in working a mine is drink! and that especially in parts where the sale of spirits is interdicted. The liquors sold seem to equal in vileness the "cango" manufactured by the Boers of South Africa. The author has found from experience that a tumbler of hot tea flavoured with a slice of lemon is not only palatable and comforting, but will carry a man twice as far as any concoction of alcohol."

It would scarcely be just to the author were we to quote his interesting suggestions for the utilisation of asbestos. Suffice it to say that he has produced a most interesting and valuable monograph, which, we trust, will be duly appreciated.

Origin of the Auriferous Region of Tacuarembó, its Analogy and Concordance with Others (i.e., Ore-Regions), on the American Continent. By CLEMENTE B. POSADA. London: The Consul-General of Polina.

THE author of this work has an annoying fondness for quotation marks. We find not only names of places—some of them well known, such as Potosi, Minas Geraes, and Matto Grosso—thus enclosed, but even the names of rocks, such as dolomite, and trachyte, and basalt, and what is yet more gratuitous the names of elementary bodies, such as chlorine and hydrogen, and compounds such as chlorhydric acid and silica. "Calcium" is an element with which we have not had the opportunity of becoming acquainted. What, further, we must ask is an "albant" condition?

Of sulphur it is said "How can one otherwise conceive that sulphur was not to be found among them (the elements), which is of so volatile a nature, when even now-a-days we see it adhere tenaciously to electricity, which seems to be its necessary attendant following in all its evolutions, and even at the moment when it huris itself upon the earth in the form of the lightning's flash or the thunderbolt."

Don Barrial Posada appears—as far as we can understand his extraordinary language—to be a believer in the catastrophie geology of the past. He speaks of the "ossaries of the existences ship-wrecked in the world in which they lived," of the "arterial and venous (sic) system of the *saxus igneus* (igneous rocks)" "Azote," the author pronounces "more abundant, more sensitive, and subtil than oxygen." To electricity he decidedly assigns a material, ponderable character, as one of the elements. He speaks of "the vast ocean of igneous electrical liquid,

gaseous and electro-dynamic substances." Such utterances and many more which we might quote, even if translated into the Queen's English and freed from typographical errors, form a curious introduction to a work essentially industrial and technical, and which seems intended to convince European capitalists that there is ample room for them to invest in the gold mines of Tacuarembó. Of the room we do not doubt, but to pronounce on the probable returns we must leave to our financial contemporaries.

We will merely quote the following statement.

"The region of New Granada, which comprises nine districts, and which we may consider of equal or even more importance than that of California, is less so than that of Matto Grosso, and this is not richer than the region of Tacuarembó." If either New Granada, or Matto Grosso, or Tacuarembó can put out as much mineral wealth as California, the fact will soon speak loudly for itself.

Statistical Returns of the Commerce, Navigation, &c., of the Republic of Uruguay for the Year 1889. Issued by Authority of the Consul-General of Uruguay. London: Dunlop and Co.

THIS pamphlet, though containing nothing which can legitimately come under the cognisance of the CHEMICAL NEWS, is rich in matter well worth the notice of commercial journals and commercial men.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—The dilemma in which the Chemical Society is now placed may be briefly stated as follows:—

1. By continuing the *status quo*, unlimited admission of persons likely to use the letters F.C.S. as a qualification for trade purposes cannot be effectually checked.

2. By adopting any severe scrutiny of qualification, such as has been proposed, in order to prevent the evils above-mentioned, two worse misfortunes would accrue.

(a) All those at present registered as Fellows would have their position as chemists legitimatised and their competence certified—a result scarcely desirable.

(b) The original object for which the Chemical Society was founded, namely, to provide what is in effect an intellectual club for the advancement of chemistry, would be wholly frustrated, and a severe injustice done to many in all ways worthy of admission.

It appears to us that there is but one way of escape, *viz.*, that the present method of election be retained, but that the Society take immediate steps to make it publicly known that Fellowship in it confers no professional status upon the holder thereof.—We are, &c.,

A. G. BLOXAM.
BERIAM BLOUNT.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS, vol. lxii., p. 247, Messrs. Lloyd and Teed appear again, this time to return thanks for the "hundreds" of replies to their recent circular.

There is, however, a somewhat naïf admission that the "hundreds" are not quite satisfying contained in their last lines; a sort of extra thankfulness for small mercies to come in the shape of a hope for a reply from "any Fellow" who may have delayed signing the circular,

just so; the party "on the fence" is always a desirable addition at election times, and the approved method of securing him is to produce to him convincing evidence that the majority has alighted on your side. Can Messrs. Lloyd and Teed's inability to answer the "hundreds" have arisen from a feeling of this sort? Meanwhile some of us would feel greatly obliged if the authors of the document would answer the following little query, *viz.*:—How many of the "hundreds" who answered the circular did so under the idea (fostered by its remarkable resemblance in type and paper to official Chemical Society notices), that it was a communication from the secretaries, and accordingly returned the circular to *them* at Burlington House.—I am, &c.,

R. J. FRISWELL.

THE PREVALENCE OF COPPER IN CEREALS.

To the Editor of the Chemical News.

SIR,—Mr. Johnstone's remarks in the CHEMICAL NEWS (vol. lxii., p. 247), reminds me of a similar experience I had in the year 1878. I had prepared two tons of malt syrup with great care. Dr. Atfield stated it contained the largest proportion of diastase of any he had examined up to that date, but unfortunately it contained copper also. At first I attributed the contamination to the copper of the vacuum pan, but as this had been in constant use in the manufacture of sugar, in which no copper was found, I had to seek elsewhere. It was finally traced to the malt, which was of the finest quality I could obtain.

Being desirous of testing the soil on which the barley was grown I applied to the Mark Lane broker, from whom I purchased the malt, but nothing would induce him to give me any information on the subject. I stopped the manufacture and used up the syrup in feeding my pigs, who, notwithstanding the presence of copper to considerable extent, thrived on it over a period of above twelve months.—I am, &c.,

EDWARD BEANES.

Moatlands, Paddock Wood,
Kent, Nov. 17th, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 17, October 27, 1890.

Electrolysis of Aluminium Fluoride by Igneous Fusion.—Adolphe Minet.—The author has shown in previous papers (*Comptes Rendus*, February 17th, and June 9th, 1889) that he has produced aluminium by the electrolysis of its fluoride in a state of fusion. He now gives the composition of the electrolytic bath which yields the best results at given temperatures, and at a given density of current at the electrodes. The bath is formed of a mixture of sodium chloride and double aluminium sodium fluoride, corresponding to the chemical formula (expressed in equivalents) $6\text{NaCl} + \text{Al}_2\text{F}_3 \cdot 3\text{NaF}$. The melting-point was 675° ; the point of the emission of vapours 1035° ; specific gravity at 820° , 1.76; coefficient of expansion in the melted state 5×10^{-4} ; electric conductivity at 870° 3.1.

On the Amylamines.—A. Berg.—This paper does not admit of useful abstraction.

Revue Générale des Sciences Pures et Appliquées.
Vol. i., No. 20, October 30, 1890.

Fire-Damp and its Accidents.—H. Le Chatelier.—In a general survey of the question of coal mine explosions,

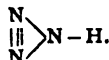
the author lays little weight upon coal dust in the absence of explosive gases. Possibly he overlooks the serious calamities produced in flour-mills by the dust of flour—a much less combustible substance—in the total absence of gaseous hydrocarbons. His chief reliance is laid on ventilation.

In an Annual Review of Physiology, by Prof. Léon Fredericq, the author mentions the fact that peptone, the normal product of the digestion of the albumenoid matters, is a true poison, which fails to prove fatal merely because it is progressively re-converted into albumenoids.

Another curious fact is that, according to Hermann, the excreta do not consist chiefly of the undigested portions of the food, but of the products of the secretion and the desquamation of the intestine.

In a review of Prof. A. Marshall's "Principles of Economics" we find the following laudable deliverance:—"The mania for elementary works, the production of the ignorant, who apologise for insufficiency of their works by the plea of being intelligible to the young, has inundated our book stores with ridiculous works. The 'manual,' the elementary book, is, in certain departments, the wound of instruction.

A New Gas, Azothydric Acid.—Prof. Curtius, of Kiel, has obtained a compound, N_3H , for which he proposes the constitutional formula—



It is very soluble in water, and the solution dissolves zinc, copper, and iron, with evolution of hydrogen and the formation of nitrides, in which the metals are substituted for the hydrogen set free.

MISCELLANEOUS.

The Determination of Fat in Milk.—The Dairy Association of Kiel offers a prize of £150 (3000 marks), for an improved method for determining the fatty matter in new milk, skimmed milk, and butter milk, without the use of a chemical balance as accurately as by the gravimetric process. It must be free from danger, cheap, and so simple in execution as to allow of comparative determinations of the fat in the milk of individual cows; and it must be distinctly preferable to all the methods now in use. Applications marked with a motto and accompanied with a sealed envelope containing the name and address of the sender, and with the apparatus required, may be addressed to Herr C. Boysen, Kiel, up to October 1st, 1891.

The Sale of Poisons.—From a circular sent out under the auspices of the British Medical Association, it appears that certain physicians and surgeons are dissatisfied with the existing state of the law on the sale of poisons. The first point urged in objection to the present law is that "the present poison schedule includes only a limited number of substances, many well-known and powerful poisons, notably the mineral acids." We submit that any restriction upon the sale of the mineral acids, the most commonly used of all reagents, could not fail to act as a check upon chemical research. Against any such interference we protest most earnestly, and trust that our protest will be followed by that of our scientific contemporaries, and by that of the Fellows of the Chemical Society and of the Institute of Chemistry. It would be indeed deplorable if chemistry in Britain should be fettered and humiliated in a manner similar to that which has befallen physiology. The fatal accidents from poisoning in this country are not so numerous as to furnish any *raison d'être* for a new agitation, whilst at the same time no more stringent regulations are asked for

concerning the common sale of revolvers, which have far fewer legitimate uses than poisons, which occasion far more mischief, and which now readily find their way into the hands of burglars, madmen, conspirators, and heedless boys. We should be strongly in favour of the proposal to restrict the sale of poisons, quack medicines, and indeed of all "patent" or proprietary nostrums, to the pharmacist. At present they are sold chiefly by grocers, oilmen, and even by house-furnishers and "general providers."

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Medical, 8.30.
Society of Arts, 8. (Cantor Lectures). "Gaseous Illuminants," by Prof. Vivian B. Lewes.
TUESDAY, 25th.—Royal Medical and Chirurgical, 8.30.
Institute of Civil Engineers, 8.
WEDNESDAY, 26th.—Geological, 8.
Society of Arts, 8. "Physical Tests in Competitive Examinations," by Francis Galton F.R.S.
THURSDAY, 27th.—Royal, 4.30.
Institute of Electrical Engineers, 8.
FRIDAY, 28th.—Physical, 5. "Notes on Secondary Batteries," by Dr. Gladstone and Mr. W. Hibbert. "An Illustration of Ewing's Theory of Induced Magnetism," by Prof. S. P. Thompson.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1618.

NOTE ON PRIESTLEY'S METHOD OF MEASURING OXYGEN IN AIR.

By J. ALFRED WANKLYN.

PRIESTLEY'S method of measuring the oxygen in the air is certainly the quickest, and is easy of execution, and is accurate when properly carried out; indeed there are possibilities of accuracy in this method which promise to place it in that respect before every other. It is the oldest, or at any rate one of the oldest, methods of measuring oxygen, dating almost as far back as the discovery of oxygen itself.

I have an old book open before me, date of publication 1806. Turning to the article "Eudiometer," I read—

"The eudiometers proposed by different chemists may be reduced to five.

"1. The first eudiometer was made in consequence of Dr. Priestley's discovery that when nitrous gas is mixed with air over water, the bulk of the mixture diminishes rapidly in consequence of the combination of the gas with the oxygen of the air and the absorption of the nitric acid thus formed by the water." . . . "Dr. Priestley's method was to mix together equal bulks of air and nitrous gas in a low jar, and then to transfer the mixture into a graduated glass tube about three feet long in order to measure the diminution of bulk." The article goes on to refer to the work of Falconer, of Bath, Fontana, Cavendish, and Humboldt, and then concludes, "But after all the exertions of these philosophers, the method of analysing air by means of nitrous gas is liable to so many anomalies that it cannot be depended upon."

Further on we learn that "the result of the numerous experiments which have been made with nitrous gas is that the proportion of oxygen in atmospheric air varies in different places and at different times." And the maximum percentage of oxygen in air is given at 30 per cent, the minimum at 22 per cent.

"2. The second kind of eudiometer was proposed by Volta," and the account goes on to state that this explosion of air mixed with hydrogen gas, and Volta's method is condemned even more emphatically than Priestley's.

Three other methods of measuring the oxygen in air are then described and approved of. Such was the state of the chemist's knowledge in 1806—thirty years after the discovery of oxygen. Since that date, Volta's method by explosion with hydrogen gas has risen into favour, and in Bunsen's classical work on "Gasometry," published in 1857, occupies the post of honour. The vindication of Priestley's method has been long delayed, even until the year 1890. The question suggests itself why did the Priestley method fail in the early days? The answer is not far to seek. This method failed because the manipulation was wrong. Water holds oxygen in solution, and the circumstances of the old experiments were such that the oxide of nitrogen employed in the experiments expended itself partly in combining with the oxygen dissolved by the water. The mixture of equal bulks of oxide of nitrogen and air in a low jar, and then the direction to transfer to a graduated tube about three feet long, points plainly enough to the employment of large volumes of water. Operating in that manner the operator is bound to mistake the oxygen dissolved by the water for the oxygen of the air, and consequently to arrive at too high a figure for the oxygen of the air.

If the reader will now turn to the description given in the air analysis recently published, he will perceive that

by the employment of the Hempel apparatus as therein described, this source of error is avoided. The directions are to measure the air in the gas-burette, and then to pass it into an absorption-pipette containing water. Then the oxide of nitrogen is introduced into the gas-burette and measured, and then (without bubbling through water) immediately passed to the air in the absorption-pipette. The nitric peroxide fumes which result are rapidly absorbed by the water in the absorption-pipette, and the gas is passed back and measured in the gas-burette. In short, in the Priestley process as now carried out, there is no mistaking oxygen dissolved for oxygen in the air; hence the success of the method in our hands.

ON THE SPECIFIC HEATS OF GASES AT CONSTANT VOLUME.

PART I.—AIR, CARBON DIOXIDE, AND HYDROGEN.*

By J. JOLY, M.A., B.E., Assistant to the Professor of Civil Engineering, Trinity College, Dublin.

IN this first notice the specific heats at constant volumes of air, carbon dioxide, and hydrogen are treated over pressures ranging from seven to twenty-five atmospheres. The range of temperature is not sensibly varied. It is found that the specific heats of these gases are not constant, but are variable with the density. In the case of air the departure from constancy is small and positive; that is, the specific heat increases with increase of the density. The experiments afford directly the mean value 0.1721 for the specific heat of air at the absolute density of 0.0205, corresponding to the pressure of 19.51 atmospheres. A formula based on the variation of the specific heat with density observed in the experiments ascribes the value 0.1715 for the specific heat at the pressure of one atmosphere. The formula assumes the specific heat to be a linear function of the density, which must as yet be regarded only as an approximation, the exact nature of the relation being concealed by variations among the experiments.

These results appear to be in harmony with the experiments of Wiedemann on the specific heat at constant pressure, and of Rowland on the mechanical equivalent of heat, from which the value 0.1712 is deduced for C_v at 760 m.m.

The experiments on carbon dioxide reveal a more rapid variation of the specific heat with density, the variation in this case being again positive in sign. The formula—

$$C_v = \rho \times 0.2064 + 0.16577$$

appears with considerable reliability to express the relation between specific heat and density.

The relation between specific heat and density in the case of hydrogen is of a negative character; that is, the specific heat diminishes with increase of density. The experiments are chiefly directed to elucidate this point, for, owing to the difficulty of preparing pure hydrogen, it was found that variations in the quantitative results of experiments on different samples of the gas were unavoidable. Accordingly the experiments were directed to a comparison of the specific heats of like samples of the gas at different densities. The variation with density is small, but (with one exception) all experiments on the purer hydrogen ascribe a negative character to it.

The nature of these variations of specific heat with change of density is, in the case of the three gases, in accord with their behaviour as regards Boyle's law, within the limits of pressure.

The experiments were effected in the steam calorimeter, a differential method being used in which an empty or idle vessel is thermally compared with the vessel holding the gas at high pressure. The vessels possessing ap-

* Abstract of a paper read before the Royal Society, Nov. 20, 1890.

proximately the same calorific capacity, the result, theoretically, is as if the gas was dealt with isolated from any containing vessel. Although practically this is not attained many sources of error are eliminated by the procedure adopted.

ACTION OF NATURAL ORGANIC COMPOUNDS ON IRON PLATES.

By Dr. T. L. PHIPSON, F.C.S., &c.

SOME little time ago M. L. Vignon called attention to the action of tannin upon iron plates when this substance is used as an anti-incrustator in boilers. He expressed the opinion that it was injurious to boilers on account of its corrosive action. Latterly this opinion has been attacked by Mr. L. Manstetten, who has made some experiments on a small scale, and concludes that the action is not of much consequence, as the quantity of iron taken up from iron vessels used in the extraction of tannin materials is very small, &c.

I am of opinion that M. L. Vignon is right, and that the use of glucosides as anti-incrustators may be fraught with much danger to the iron plates of a boiler. I may refer to the corrosive action of the leaves and stalks of the Virginia creeper upon iron netting, when they are battered by the wind and rain against the metallic surface. It is surprising in how short a time the netting is utterly destroyed. I alluded to the subject in a note published in the *CHEMICAL NEWS* a few years ago. It is true that the juice of that plant is very acid, but perhaps, not much more so than many decoctions of tannin materials, and I think the greatest caution should be used in applying vegetable extracts of any kind as anti-incrustators for iron boilers on account of their evident tendency to develop acids, and to corrode the plates.

THE SYNTHESIS OF UREA.

By F. E. MATTHEWS.

ALTHOUGH the credit for the first synthesis of an organic substance from inorganic material must be given to Wöhler on account of his synthesis of urea, in 1828, yet it is an interesting fact which appears to have escaped notice, that this substance was produced by John Davy as early as 1811 or 1812 from purely inorganic substances.

Unfortunately Davy did not sufficiently investigate the product he obtained, which was a mixture of ammonium chloride and urea, or the study of organic synthesis would have been accelerated by a period of 16 years.

In the *Philosophical Transactions* for 1812 the following paper appears:—"On a Gaseous Compound of Carbonic Oxide and Chlorine. By John Davy. Communicated by Sir Humphry Davy, Knt., LL.D., Sec. R.S. Read February 6, 1812."

The quotations here given are taken from the *Abstracts of the Philosophical Transactions*, and the account does not differ materially from that in the original paper.

"Although it has been asserted by Messrs. Gay-Lussac and Thenard, and also by Mr. Murray, that carbonic acid (this is a misprint for carbonic oxide, which occurs in the original) and chlorine have no action upon each other, Mr. J. Davy has observed the contrary to be the case. A mixture of equal parts of these gases, previously dried over mercury, being exposed to bright sunshine for about one quarter of an hour, lost all colour of the chloric gas, and were found condensed into half their former volume. The smell of the gas was more suffocating than that of chlorine. It occasioned a very painful sensation in the eyes; it reddened litmus-paper; it combined with ammonia, forming a salt perfectly neutral and dry, but deliquescent, by

attracting moisture from the atmosphere. This salt was decomposed by sulphuric, nitric, and phosphoric acids, and also by liquid muriatic acid; but sublimed unaltered in carbonic, sulphurous, and muriatic acid gases.

"In those instances where the salt was decomposed, the products were carbonic and muriatic acid gases. It is remarkable, that in the formation of this ammoniacal salt the new gas combines with as much as four times its bulk of ammoniacal gas."

The last paragraph quoted contains sufficient detail to show that Davy must have synthesised urea, the equation for its formation being—



In Roscoe and Schorlemmer's treatise (New Edition, vol. i., p. 647) the references given for the synthesis of urea by the action of ammonia upon carbonyl chloride are Nathanson, *Ann. Chem. Pharm.*, xcvi., 287; Neubauer, *Ibid.*, ci., 342.

Royal Indian Engineering College,
Cooper's Hill, Staines.

NOTES ON SOME HOT SPRING WATERS.*

By A. LIVERSIDGE, M.A., F.R.S., Professor of Chemistry,
University of Sydney.

(a). Note upon the Hot Spring Waters, Ferguson Island, D'Entrecasteaux Group.

THE specimens forming the subject of this note were collected by Sir W. Macgregor, K.C.M.G., Governor of British New Guinea, who thought that these waters might prove to be of scientific interest, and therefore forwarded them to me for examination.

Accompanying the specimens was the following description of the hot springs, prepared by Mr. Basil Thomson, together with two photographs of the locality:—

"The evidence of volcanic action on the east end of Ferguson and Goulvain Islands in the D'Entrecasteaux Group were plainly visible from the sea, but a few miles to the westward gave place to a schistose slaty formation, of which the island seems mainly composed. It was therefore with no little surprise that, on the evening of our anchoring in Seymour Bay, we noticed a strong smell of sulphur, the fumes being sufficient to discolour the white paint on the vessel during the night. Seymour Bay lies in the narrow straight named by Captain Moresby after himself, and is fringed with mangrove and dense scrub and backed by low hills.

After forcing our way through mangrove and sago swamps for about half a mile, we came on a well-beaten native path, which led to a rapid stream. Some of the party who stopped to prospect for gold, found the gravel in the bed of the stream too hot for the hands, although the water of the stream was cold.

Making our way southward, we emerged from dense scrub upon a flat, bare of vegetation, and dotted with little hillocks of pure sulphur, from which vapour was rising.

The vegetation surrounding this flat was identical with that in the non-volcanic country, and terminated suddenly, but on the flat itself a few eucalypts were trying to exist. This is the most easterly point at which this tree was found in British New Guinea.

Passing over this flat, which gave a hollow sound to the feet, showing that the crust was very thin, we climbed a low hill, and looked down upon a small lake shut in by hills, having a margin of dazzling whiteness, made by the crystallisation of salts, which tasted strongly of alum. At the foot of the hill was a spring of boiling water, which discharged into the lagoon.

* From the *Transactions of the Australasian Association for the Advancement of Science*, Melbourne Meeting, 1890, Section B.

The low hills surrounding the lake were composed of sulphur and the white salt referred to above. The water of the lake, which was covered with wild fowl, was of a light yellow colour, and tepid, and the margin was surrounded by a thin crust, which gave way when trodden on, and let one of our party through into three feet of black slime.

All round the base of the hills was a succession of holes full of boiling mud. Near the summit of one of the low hills we found a larger hole, which was throwing up liquid mud to the height of several feet with loud reports. (Photograph enclosed).

Further to the northward we found a similar lake and hot springs, and some of our party, who were obliged by the hostility of the natives to pass the night on the top of one of the sulphur hills, experienced much inconvenience from the fumes. At night the hills give out a bluish light.

(Signed) B. H. THOMSON."

Sydney, 8th March, 1889.

None of the specimens were in sufficient quantity to permit of a full analysis being made of their mineral constituents, the largest samples being contained in a so-called quart brandy bottle.

The only quantitative determinations which could be conveniently made were the total solids, fixed solids, loss on ignition, and chlorine and sulphuric acid.

The loss on ignition includes any organic matter which may have been present, water of combination, volatile and decomposable salts, together with some sulphur.

There were four samples in all.

SAMPLE No. 1.—Labelled "*Seymour Bay, Ferguson Island 11th November, 1888. Boiling Water from Hot Spring.*"

This sample was contained in a soda-water bottle, and as one-half of it consisted of solid matter, it would be more correctly described as a mud.

The sediment, or solid matter, was of a bluish grey colour, and was found to contain a few diatom frustules and small crystals of selenite (calcium sulphate), and a good deal of sulphur. At some future time it is intended to make a more complete examination of this sediment, as there is sufficient for a quantitative analysis.

The sulphur was carefully tested for selenium, but none was found to be present; neither did this residue contain either arsenic or phosphorus.

The supernatant liquid was filtered off from the mud after allowing the specimen to stand for two or three days; the filtrate had a strong smell of sulphurous acid, and strongly reddened blue litmus-paper, showing the presence of free acid, and, on exposure to the air, soon became milky from the separation of sulphur.

On evaporating the filtrate down to dryness in a platinum dish over a water-bath, a pale brownish residue was left, which rapidly absorbed moisture. On ignition it intumesced strongly, and gave off dense white acid fumes (of sulphur trioxide), the ignited residue being yellow when hot and brown when cold.

The weighings gave—

Loss on ignition . . .	9.63 parts per 1000
Fixed solids . . .	4.47 " "
Total solids . . .	14.10 " "

The chlorine and sulphuric acid were not determined in this sample. The fixed solids left on ignition were found to contain both soluble and insoluble silica—sufficient of the former to gelatinise with hydrochloric acid—much iron, mainly present in the original water in the ferrous condition, some magnesia, lime, and a considerable quantity of sodium chloride.

Lithium was sought for, but no indication of it was obtained, although the other three samples gave the lithium band most readily.

SAMPLE No. 2.—Labelled "*Hot Springs, Seymour Bay, 11th November, 1888. Water after Boiling.*" Contained in an ordinary pickle bottle.

This also showed a large amount of a powdery yellow sediment, about 10 per cent perhaps, which consisted mainly of free sulphur.

The water contained a good deal of free sulphuric acid, and on evaporating down to dryness over a water-bath, the residue blackened from the action of the free sulphuric acid upon the organic matter present, and on ignition copious fumes of sulphur trioxide were evolved. Much gelatinous silica was left, together with iron, lime, magnesia, and soda. This residue showed a well-marked lithium band.

The iron was present in the original water mainly in the ferrous state.

Loss on ignition . . .	1.274 parts per 1000
Fixed solids . . .	3.630 " "
Total solids . . .	4.904 " "
Chlorine . . .	1.240 " "

SAMPLE No. 3.—Labelled "*Seymour Bay, 11th November, 1888. Boiling Water from Small Spring.*" Contained in a soda-water bottle.

This, like No. 2, contained a yellow powdery sediment of sulphur and other matters. It possessed a strong acid reaction, and gave off a smell of sulphurous acid, together with that of sulphuretted hydrogen.

On evaporating down to dryness, a light coloured residue was left, brown in the centre, and on ignition this blackened considerably, but only gave off a small quantity of sulphur trioxide fumes. The salts present were the same as in No. 2, and the lithium band was equally well marked.

Loss on ignition . . .	0.630 parts per 1000
Fixed solids . . .	4.470 " "
Total solids . . .	3.100 " "
Chlorine . . .	0.730 " "

SAMPLE No. 4.—Labelled "*Seymour Bay, 11th November, 1888. Water from Lagoon, Hot Springs, Saline Lake, margin surrounded by sulphur.*" Contained in a wine bottle.

The sediment from this was but small in amount, and of a dark brown colour. There was also a little black flocculent matter. The water possessed a strong acid reaction, and smelt of sulphuretted hydrogen.

On evaporating down to dryness, a large quantity of iron was found to be present, mostly in the ferrous condition, much gelatinous silica, some lime, magnesia, and soda, together with lithium.

On ignition, the residue became intensely black, gave off slight fumes with an acid reaction and decrepitated (from sodium chloride crystals), and left a dark ferruginous-looking residue.

Loss on ignition . . .	2.110 parts per 1000
Fixed solids . . .	5.470 " "
Total solids . . .	7.580 " "
Chlorine . . .	1.390 " "

These waters present the usual characters of hot spring waters occurring under similar conditions, and require no special comment except as to the presence of lithium, and I regret that none of the samples were sufficient to allow the amount of this element to be estimated; but, perhaps, on some future occasion it may be possible to bring away a larger supply of the water, or in default of that, the residue left by the careful evaporation (on the spot) of a fair quantity of the water.

Lithium was formerly regarded as a very rare element, but the spectroscopic shows that, although it only occurs in small quantities, it is one of the most widely distributed elements, and is found in many minerals, rocks, soils, and in the ashes of numerous plants.

It may prove to be present in these waters in sufficient quantity to render them useful at some future time, for either medicinal or other purposes.

(b). *Note on Water from a Hot Spring, Savo Island, Solomon Group.*

This specimen, received from Mr. Charles M. Woodford, in February, 1889, was contained in an ordinary fruit bottle.

On opening the bottle, a strong smell of sulphuretted hydrogen was emitted, and the gas continued to escape for two or three days, the sides of the measuring flask were marked by small bubbles of the gas as it slowly escaped, and the previously clear water became milky from the deposition of sulphur.

The bottle contained rather a large amount of black sediment, which, under the microscope, was seen to consist of black opaque granular masses, fragments of quartz and other transparent mineral, together with a few diatom frustules; the black particles were soluble in hydrochloric acid and gave off sulphuretted hydrogen, and the solution reacted for iron; hence they were proved to consist of iron sulphide, probably of quite recent origin, just as is seen in the New Zealand hot springs. (Liver-side, New Zealand Hot Springs, *Four. Roy. Soc. of N.S.W.*, 1887).

With litmus paper the reaction of the water was slightly acid, as might be expected.

The clear water, on decantation, after long standing, so as to be free from sediment, was found to contain 0.764 grms. of total solids per litre (53.48 grains per gallon) in solution, and after ignition 0.422 grms. (29.54 grains per gallon of fixed solids per litre).

The residue left on evaporation was whitish, with a silky lustre, and emitted an odour of sulphur compounds, as is usual in such water residues; and on ignition gave off much steam from water of combination. It rapidly blackened, and the carbonaceous matter present burnt off but slowly.

The amount of water at my disposal rendered it impossible to make a quantitative analysis of the salts in solution, but the qualitative analysis showed the presence of hydrochloric, sulphuric, and sulphydric acids, together with silica, the metals iron, aluminium, calcium, magnesium, and sodium, and ferrous sulphide, as already mentioned.

As far as can be ascertained from the above necessarily imperfect examination, there is nothing unusual in the character of the water; the spectroscope did not show the presence of any of the rarer alkaline metals, such as lithium. A much larger quantity of the water would be required to make a satisfactory examination for them, but there was quite sufficient of the water to show that they are not present in any quantity.

The following notes are appended, as it may be of interest to some of the members to have the accounts of other Pacific hot spring waters for comparison.*

Samples of Water from the Island of Simbo and Santa Anna. Collected by Dr. H. B. GURFFY, Surgeon, H.M.S. *Lark*.

Bottle 49.—Containing water from the fresh-water lake of Wailava, in the Island of Santa Anna, collected in April, 1882. I have seen no reference to this lake in any of the works which bear on these islands. The Island of Santa Anna has the character of a raised atoll, with the large central depression occupied at its lowest part by the waters of the lakes of Wailava and Waipiapia. Wailava is about half-a-mile across in length, and has a depth of 15 fathoms, as ascertained by Lieut. Oldham. On carefully examining this lake, I found that its waters are at about the sea level, though they are not affected by the rise and fall of the tides. On one side it is only separated from the sea by a low, swampy tract about one-third of a mile across, and not elevated more than 20 feet above the

sea. The surface of this tract is strewn with coral fragments, and the more swampy portion abounds with *Auricula*. It is evident that this lake has been only cut off from the sea by recent elevation. On making a rough examination, I found the density about that of fresh water, with *chlorines* abundant, *lime* two or three grains per gallon, *ammonia* unmistakable, *taste* flat and fresh. The water rapidly decolourises a solution of permanganate of potash.

Bottles 142 and 143.—Containing water from the boiling spring in the island of Simbo, collected in May, 1882. The island of Simbo is formed of trachytic rocks, and contains in the southern part an extinct crater, a solfatara, and numerous fumaroles, which pierce the rocks, occurring from the sea up to the highest summit, about 1100 feet above the sea. This water was collected from the boiling spring on the shores of a lagoon (very probably an old crater) on the south-west side of the island. The spring is placed amongst decomposed trachytic rocks, a foot or two above the sea level. Its temperature is 212°, and large quantities of H₂S are exhaled. Iron oxide stains the rocks around, which are encrusted with sulphur and chloride of sodium in some places. Numerous fumaroles pierce the slopes overlooking the springs: sulphur, alum, milk-white opal, &c., from deposits around their orifices. As this spring is close to the edge of the lagoon of salt water, with the tidal movements of which its waters rise and fall, I am of opinion, from a cursory examination of the water, that its composition may be regarded as sea water, plus the substances discharged by a fumarole.

Bottle 150.—Water condensed from one of the fumaroles in the solfatara on the south-west point of Simbo, in May, 1882. A little sulphur, which unavoidably fell in, forms a sediment at the bottom of the bottle. For two hours the thermometer retained in the orifice of the fumarole varied only between 208° and 210° F. Watery vapour, sulphuretted hydrogen, and sulphurous acid were evolved, flaky crystals of sulphur encrusting the sides of the aperture. A strip of paper, soaked in a solution of acetate of lead, was immediately blackened, and the black metallic silver sulphide was formed in the interior of a piece of glass-tubing, moistened with silver nitrate, whilst the presence of sulphurous acid appeared to be indicated by the suffocating smell of burning sulphur, by the presence of sulphur deposits, and by the reddening of litmus paper. No turbidity was produced in lime-water, nor was the presence of hydrochloric acid gas shown on exposing a solution of silver nitrate.

The interior of the solfatara was whitened by the decomposing influence of the vapours evolved. The elevation of the fumarole in question was rather under 300 feet above the sea.

Bottle 151.—Water condensed May, 1882, from one of the fumaroles on the summit of the South Hill, in the island of Simbo, elevated about 1100 feet above the sea. The temperature of the fumarole varied during two hours between 175° and 180° F. Employing the same rough field tests, I ascertained that watery vapour was the principal substance discharged. No effect was produced on acetate of lead, silver nitrate, or lime-water, and litmus paper was very slightly reddened after a prolonged exposure. No deposits were formed around the orifices of the fumaroles on this hill summit. The trachytic rock was much decomposed, and a little of the decomposed rock unavoidably fell in, and forms a sediment at the bottom of the bottle.

For an additional example of water from hot springs at Suva, Fiji, see "At Home in Fiji," by F. M. Gordon Cumming.

Exsiccators.—R. Frubling (*Zeitschrift Angewandte Chemie*) proposes an instrument which differs from the ordinary form merely by its greater diameter. C. Liebermann (*Berichte*) uses exsiccators of yellow glass for bodies which are affected by light.

* *Journal of the Roy. Soc. of N.S.W.* for 1887, vol. xi., p. 223.

AUSTRALIAN METEORITES.*

By A. LIVERSIDGE, M.A., F.R.S., Professor of Chemistry,
University of Sydney.
(ABSTRACT).

THE *Thunda meteorite*, found near Windorali in the Diamantina district, Queensland.—The mass received by me originally weighed 137 lbs., and the specific gravity is 7.78. In composition it consists essentially of nickeliferous iron, containing a trace of cobalt, together with a little sulphur, phosphorus, and carbon. The crystalline structure is extremely well marked, which is not only shown by the fractured surface, but by the cut and polished sections when etched by acids, bromine, or copper sulphate. This meteorite is also remarkable for the many nodules of sulphide of iron which it contains, from which fissures proceed in such a way as to show that the iron sulphide must have crystallised last; in fact, it looks as if it had been the cause of the fissures.

Barratta Meteorites, Nos. 2 and 3.—The first meteorite found at Barratta, near Deniliquin, in New South Wales, has already been described in the *Journal of the Royal Society of New South Wales* for 1872 and 1880.

These later ones, also in the possession of Mr. Russell, F.R.S., Government Astronomer, Sydney, were found near the site of the first; the second one has a weight of 31 lbs., and a specific gravity of 3.706; the third weighs 48 lbs., and has a specific gravity of 3.429; the first having a specific gravity of 3.429. In structure and appearance all three are very much alike, and they consist essentially of silicates of magnesia (as enstatite), iron, with small quantities of other substances, intermingled with a network of nickeliferous iron.

Gilgoi meteorite, in the possession of Mr. Russell, F.R.S., Government Astronomer, Sydney, found on the station of that name, near Brewarrina, N.S.W.—This weighs 67½ lbs., and has a specific gravity of 3.857. It is very much more cracked and fissured, and contains rather a larger proportion of nickeliferous iron than the preceding one, but in other respects closely resembles them.

Eli Elwah—This meteorite is also an earthy one, containing nickeliferous iron, with a chondritic or granular structure; it weighs 33½ lbs., and has a specific gravity of 3.537.

Photographs and micro-photographs of sections of the four earthy meteorites were shown, as well as specimens of each.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, November 6th, 1890.

SIR.—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to

organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, the whole were found to be clear, bright, and well filtered.

Throughout the month of October the character of the water supply to the metropolis continued to be entirely satisfactory, in respect alike to freedom from turbidity, from colour-tint, and from any excess of organic matter. The mean proportion of organic carbon present in the Thames-derived water was only 0.136 part in 100,000 parts, with a maximum of 0.160 part in any single sample examined. The mean ratio of brown to blue tint of the same water was as 10.4 : 20.0; while the mean amount of oxygen taken up in the oxidation of the organic matter present in a gallon of the water was just under 0.4 grain.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE ATOMIC WEIGHT OF MAGNESIUM AS DETERMINED BY THE COMPOSITION OF ITS OXIDE.

By W. M. BURTON and L. D. VORCE.

THE method employed by Dr. H. N. Morse* and one of us (B.) for the preparation of pure zinc and the determination of its atomic weight yielded such satisfactory results that it seemed desirable to employ the same process for the purification of other metals and for the re-determination of their atomic weights. Among others, magnesium was suggested as being suitable for the purpose, because, like zinc, it can be distilled at a comparatively low temperature, and its nitrate upon ignition yields an oxide of definite composition and stable when heated to a very high temperature.

Therefore, in accordance with an understanding with Dr. Morse, we have undertaken the re-determination of its atomic weight. Several investigators have determined the atomic weight of magnesium, but in almost every instance either some impurity was found to exist in the materials used, or else some defect was discovered in the method employed, thereby creating doubt as to the accuracy of the results obtained. The following methods have been used:—

1. Composition of sulphate by action of sulphuric acid on the oxide (Berzelius,† Bahr,‡ Svanberg and Nordenfeldt,§ and Marignac||).

2. Determination of sulphuric acid in the sulphate by precipitation as barium sulphate (Scheerer,¶ Jacquelin,‡‡ and Gay-Lussac††).

3. Conversion of oxalate into oxide by ignition (Svanberg and Nordenfeldt‡‡).

4. Conversion of sulphate into oxide by ignition (Gay-Lussac§§).

* *American Chemical Journal*, x., 312.

† *Pogg. Ann.*, viii., 188.

‡ *Jour. f. pr. Chem.*, lvi., 310.

§ *Ibid.*, xlv., 474.

|| *Ann. ch. phys.* (6), i., 321.

¶ *Pogg. Ann.*, lxi., 535.

‡‡ *Ann. ch. phys.* (3), xxxii., 202.

†† *Ibid.*, (2), xlii., 308.

§§ *Jour. f. pr. Chem.*, x'v., 474.

|| *Loc. cit.*

* From the *Transactions of the Australasian Association for the Advancement of Science*, Melbourne Meeting, 1890, Section B.

5. Determination of chlorine in magnesium chloride (Dumas*).

6. Conversion of carbonate into oxide by ignition (Marchand and Scheerer†).

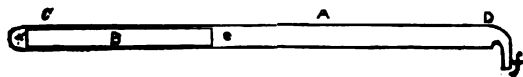
The results of these investigations are shown in the following table:—

Date.	Investigators.	At. wt. Mg. (O=16).	At. wt. Mg. (O=15.95).
1819	Gay-Lussac	22.89	22.812
1820	"	24.18	24.102
1826	Berzelius	25.20	25.122
1846	Scheerer	24.11	24.032
1847	{ Svanberg Nordenfeldt	24.63	24.562
1850	Jacquelin	24.11	24.032
1850	{ Marchand Scheerer	23.96	23.882
1852	Bahr	24.74	24.662
1859	Dumas	24.48	24.502
1884	Marignac	24.38	24.302

The method which we propose is essentially the same as that which was used in the determination of the atomic weight of zinc, and previously described in the *American Chemical Journal*.‡ Slight changes have been made in some details of the manipulation, and these will be noted in their appropriate places. The magnesium was purified by distillation in a vacuum. Weighed portions of the metal were converted into the nitrate, which was ignited to the oxide, first in a hot-air bath, and finally at the highest temperature obtainable in a muffle furnace. The simplicity and directness of the method are strong points in its favour, and we believe we have eliminated the two general difficulties by which the accurate determination of the atomic weight of magnesium has been beset, viz., first, presence of impurities in the materials used; second, the error involved in determining these impurities and correcting for them.

I. The Preparation of Pure Magnesium.

When an attempt was made to distil the magnesium in ordinary hard glass tubes, it was found that the vapours of the metal attacked the glass, forming a black voluminous substance which evolved a spontaneously inflammable gas when treated with an acid. The action of magnesium powder on silica and other oxides has been studied by Gattermann,§ and his results lead us to conclude that the black substance which we obtained was magnesium silicide of the formula Mg_2Si , and the explo-



sive gas was undoubtedly silicon tetrahydride. Further, when the silicide was dissolved in acid, there remained a yellow substance which probably was the suboxide of silicon described by Mabery.|| Repeated fractional distillation did not entirely separate this silicide of magnesium from the pure metal. In consideration of the fact that magnesium forms no alloys with iron, the idea suggested itself of using an iron tube inside the glass tube. Fig. 1 represents the method of arrangement. A is a tube of hardest potassa glass, fused together at one end. B is a tube made of thin sheet iron of the best quality obtainable. The iron tube was pushed into the glass tube as represented and then filled with small pieces of magnesium ribbon. The end of the iron tube at C is bent over in such a way as to prevent the carrying over of small pieces of magnesium during the distillation. About 10 grms. of the metal were used in each charge.

The glass tube was connected at f with a Sprengel air-pump and the apparatus thoroughly exhausted. The tube was heated in a combustion furnace throughout its whole length, but most strongly at B. When the iron tube showed a bright red heat the magnesium commenced to volatilise and sublime on the cooler portions of the tube at A, forming at first a black mirror of magnesium silicide.

Our first plan was to use an iron tube extending from C to D, so that the glass would be entirely protected from the vapours of magnesium, but numerous experiments showed that the first coating at A entirely protected the glass, so that subsequent portions of the metal were deposited without being contaminated with the silicide. Experiment also showed that the iron tube served to support the walls of the glass tube, as the latter would otherwise collapse when heated to the fusing point of magnesium. The tube at B was maintained at a bright red heat for about an hour, the gas was then turned down and the apparatus cooled very slowly. By taking proper precautions the cracking of the tube was prevented during the cooling process, thereby maintaining a vacuum in the apparatus until the end of the distillation. The portion of the metal remaining in B and that which had collected at D were rejected. The portion collected at A was three times redistilled; the magnesium which collected at A during the fourth distillation was employed for the atomic weight determination. It was deposited as a thin crystalline bar of pure white metal, which readily separated from the coating of magnesium silicide on the glass. In a few instances beautiful crystals of the metal were formed; these will be considered later in this paper. The magnesium deposited in the fourth distillation was carefully analysed, special pains being used in the tests for silicon, carbon, calcium, and iron, but we were unable to detect any impurity whatever. It was also spectroscopically examined, but the spectrum showed no lines of impurities, the characteristic green lines of magnesium being the only ones visible. We analysed the magnesium ribbon used in the distillation, and found small quantities of silicon, iron, and carbon.

II. Preparation of Pure Dilute Nitric Acid.

Pure strong nitric acid was prepared by the method already described in the *American Chemical Journal*.¶ In order that the magnesium might dissolve slowly, the nitric acid was diluted with an equal volume of water. The water was purified by distilling it first from acid permanganate of potassium, then from alkaline permanganate, and finally in the platinum apparatus which was used in preparing the nitric acid. The dilute acid was preserved in a platinum dish under a bell-jar, and a platinum spoon was used for transferring it as it was needed.

III. The Method of Procedure.

The conversion of the magnesium into its oxide was effected in porcelain crucible, the arrangement of the crucibles being the same as that described in the article on the atomic weight of zinc. A piece of magnesium weighing about 300 mgrms. was carefully broken off, and any clinging portions of dust removed by filing. A powerful lens was used in examining the metal, and it was not handled except by means of clean forceps. Having balanced a pair of crucibles with their appropriate tares, the difference in weight was noted. The piece of magnesium was then weighed into one of them, and treated with dilute nitric acid. When the metal had disappeared, the excess of acid and water was evaporated, and the nitrate of magnesium partially decomposed by heating in a sand-bath. Finally the crucibles were placed in a muffle furnace, and kept at a white heat for about two hours. After weighing, the oxide was again heated in the muffle, and as a rule one ignition was sufficient to insure constant weight. In some of the determinations,

* *Ann. ch. phys.* (3), 17, 1:9.

† *Four. f. pr. Chem.*, 1, 385.

‡ *Loc. cit.*

§ *Ber. d. Chem. Ges.*, xxii., 186.

|| *Amer. Chem. Jour.*, ix., 14.

however, two ignitions were necessary. The tares were treated with dilute nitric acid, and heated in every instance like the crucibles in which the determinations were made. The magnesium oxide was tested for oxides of nitrogen by the method described by Griess.* The magnesium oxide was dissolved in dilute sulphuric acid, and 2 c.c. each of sulphuric acid and naphthylamine hydrochlorate were added. Not a trace of the pink colour appeared. In another sample of the oxide which was not ignited to constant weight, the iodide of starch reaction for testing for nitrous acid failed to give a blue colour, while the sulphuric acid test showed a distinct pink colour.

IV. The Weighing.

The balance used was made by Becker Bros.; its capacity was 200 grms., and it was sensitive to $\frac{1}{10}$ milligramme with its full load. The balance case was enclosed in a tight-fitting wooden box furnished with appropriate doors, through which the weights and crucibles could be transferred. All observations were made with these doors closed. A gas lamp and mirror were so arranged that the ivory scale of the balance could be illuminated through a small aperture in the box; the excursions of the pointer were noted through a similar aperture situated just above the first. The methods of weighing by vibrations and of double weighing—that is, upon both pans—were employed throughout. The sensibility of the balance with the load furnished by the crucibles was determined at least once during each series of observations. Each weighing was made as rapidly as possible, allowing due time for noting observations accurately, as it is believed that an undue amount of time spent in weighing only increases the error due to changes in temperature and atmospheric conditions. Only the smaller platinum weights were used, since the magnesium oxide obtained in one experiment never weighed more than 700 m.grms. All weighings were made at night after the laboratory and streets in the vicinity had become quiet.

V. The Results.

The following table shows the result of ten successive experiments:—

Wt. of Mg.	Wt. of MgO.	At. wt. Mg. (O=16).	At. wt. Mg. (O=15.95).†
1. 0.33009	0.54766	24.278	24.202
2. 0.34512	0.57252	24.283	24.207
3. 0.26058	0.43221	24.292	24.216
4. 0.28600	0.47432	24.299	24.223
5. 0.30917	0.51273	24.301	24.225
6. 0.27636	0.45853	24.271	24.195
7. 0.36457	0.60475	24.286	24.210
8. 0.32411	0.53746	24.304	24.228
9. 0.32108	0.53263	24.284	24.208
10. 0.28323	0.46988	24.279	24.203
Mean		24.287	24.211
Highest		24.304	24.228
Lowest		24.271	24.195
Difference		0.033	0.033

If we calculate the atomic weight from the sums of the quantities of magnesium taken, and oxide obtained as recommended by Meyer and Seubert,‡ we have—

Wt. of Mg.	Wt. of MgO.	At. wt. Mg. (O=16).	At. wt. Mg. (O=15.95).
3.10031	5.14269	24.287	24.211

VI. Crystals of Magnesium.

Of the crystal form of magnesium very little is definitely known. The element is usually regarded as holohedral, hexagonal, and isomorphous with zinc and beryllium. The production of very perfect crystals during the dis-

tilation of our magnesium seemed of sufficient interest to warrant their study and description. Dr. G. H. Williams, of the Johns Hopkins University, undertook this work and kindly sent us his results for publication. The first account of magnesium crystals was given by Dumas* in 1880, who obtained them while experimenting with the gases absorbed by magnesium during distillation. Des Cloizeaux† measured these crystals and described them as hexagonal prisms with the unit pyramid and terminated by the basal plane. He obtained the axial ratio $a : c = 1 : 1.6391$.

The crystals which we obtained were about 1 m.m. in diameter, having very perfect planes, which furnished in most instances sharp and distinct reflections on the goniometer. No planes appeared except OP, P, and ∞ P. The following table shows the angles measured on four different crystals with a large Fuess goniometer. In each crystal one or more zones of 180° were observed; when more than one zone was measured the mean result is stated and the number of zones upon which this average is based is given in parenthesis.

Cryst.	OP : P.	P : ∞ P.	∞ P : P'.	P' : OP'.
I.	$61^\circ 47'$ (2)	$28^\circ 12'$ (2)	$28^\circ 17'$	$61^\circ 50'$
II.	$61^\circ 44'$	$28^\circ 15'$	$28^\circ 00'$	—
III.	$61^\circ 55'$	$28^\circ 5'$	$28^\circ 3'$	$61^\circ 57'$
IV.	$61^\circ 57'$ (3)	$28^\circ 5'$ (3)	$28^\circ 7'$ (3)	$61^\circ 52'$ (3)

The average of the twelve measurements of the angle OP : P is $61^\circ 52' 30''$; whose supplement is $118^\circ 7' 30''$. If we use this value for the axial ratio we have $a : c = 1 : 1.6202$, which is almost identical with the value obtained by Des Cloizeaux. It appears from these figures that magnesium is more closely related to beryllium, in its crystal form, than to zinc, as will be seen in the following statement:—

Beryllium $a : c = 1 : 1.5802$ Brögger.

Zinc $a : c = 1 : 1.35642$ Williams and Burton
(*Amer. Chem. Jour.*, xi, 219).

Magnesium $a : c = 1 : 1.6202$ Wilson.

Experiments were made to test the cohesive properties and slipping planes of the magnesium, but no results were obtained like those described in the investigation of zinc crystals.

It is with pleasure that we acknowledge our indebtedness to Professor Morley and Professor Mabery, who placed their laboratories at our disposal during this investigation. With such adequate facilities we were enabled to work much more rapidly and satisfactorily than we otherwise could have done.

THE DRY ASSAY OF TIN ORES.‡

PART II.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Continued from p. 170).

Class A (b).

This class embraces the bronze assays of Winkler, and the different iron assays.

4. Winkler's method§ is as follows:—5 grms. of ore are mixed with 5 grms. of cupric oxide, and charged in a clay crucible; on top are placed 15 grms. of black flux with 1.25 grms. of borax glass, then a salt cover, and finally a large piece of charcoal. The crucible is heated in a muffle or a pot-furnace, after boiling has ceased, for

* *Comptes rendus*, xc., 1027.

† *Ibid.*, xc., 1101.

‡ Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 3.

§ *Berg- und Huttenmännische Zeitung*, 1864, p. 17; also *Karl. op. cit.*, p. 483; and Balling, "Die Probirkunde," p. 391.

* *Ber. d. chem. Gesell.*, xii., 426.

† Value found by Keiser, *American Chemical Journal*, x., 249.

‡ "Die Atomgewichte der Elemente," p. 13.

three-quarters of an hour to an hour at a bright red heat, finishing the assay at almost a white heat. The result is a white brittle tin-copper alloy. With every tin assay, an assay of 5 grms. of cupric oxide with the same charge is made, and the weight of the resulting button of copper, subtracted from the bronze button, gives the weight of the tin contained in the ore.

This assay is really a modification of the German method. Its advantage is that no prills of tin (or, rather, particles of bronze) are found suspended in the slag. All the metallic oxides that have been reduced are found collected in one button. It is claimed that more tin is recovered by this method than by the regular German method, and that the buttons do not differ more than from 0.4 to 0.5 per cent. If this could be substantiated, the method would be a serious rival to the cyanide assay.

In the experiments carried out, the directions given (*ante*) were closely followed, only the black flux substitute (2 potassium carbonate and 1 flour) was used, as in the regular German method, instead of the black flux proper.

The charges were readily fusible, liquid, and showed a smooth surface when cool. The crucibles were not attacked, and no particles of bronze were discernible in the slags. As in the German assay, the upper salt slag and the lower borax slag have to be distinguished. The salt slag separates readily from the lower slag, has a crystalline structure, is brittle, has a pearly lustre, and is opaque. In the centre of every salt slag is a small cavity, into which white fern-like crystals protrude. The white base of the crystals is encircled by a green-tinged shell, and this by the bulk of the slag, which is of a lighter purple colour than that of the German assay. The reason is probably that less carbon is present in the charge, no charcoal having been added. The vitreous borax slag is hard, opaque, and greenish black. The oval bronze button is smooth, crystalline, brittle, white, and the more rounded copper button has thread-like lines of crystals on the surface, and is of a beautiful rose colour. Both separate well from their slags.

TABLE XVIII.

No. of assay.	Resulting bronze. Grms.	Resulting copper. Grms.	Resulting tin.	
			Grms.	Per cent.
95.	7.200	3.825	3.375	67.50
96.	7.170	3.805	3.305	67.30
97.	7.110	3.785	3.325	66.50
98.	7.105	3.785	3.320	66.40
99.	7.040	3.820	3.220	54.40
100.	7.020	3.770	3.250	65.00
101.	7.000	3.770	3.230	64.60
Average ..	7.092	3.794	3.298	65.96
102.	7.185	3.920	3.265	65.30
103.	7.140	3.920	3.220	64.40
Average ..	7.162	3.920	2.2425	64.85

Table XVIII. shows that too much has been claimed for this method, both as to output of tin and accuracy of results. The total average, Nos. 95 to 101 (65.96 per cent tin), is 1.88 per cent too low, and while in some cases excellent results are obtained (Nos. 95 and 96), in others, under the same conditions, an assay can be 3.24 per cent too low. It was thought that perhaps, by increasing the amount of reducing agent, better results could be obtained. Thus, 1 gm. of charcoal was mixed with the 5 grms. of ore and 5 grms. of cupric oxide, and then the usual charge given. The results (Nos. 102 and 103) show only an increase of weight in the copper recovered. Chalk lined crucibles were tried, as in the German method, but, while no essential particular could be observed in which the assay differed from that in the naked crucible, the results given in Table XIX. show that the discrepancy in the resulting weights of tin is enormous, while the output of copper is higher, and very even.

TABLE XIX.

No. of assay.	Resulting bronze. Grms.	Resulting copper. Grms.	Resulting tin.	
			Grms.	Per cent.
104.	6.850	3.815	3.035	60.70
105.	6.660	3.815	2.845	56.90
106.	6.760	3.810	2.950	59.00
107.	6.250	3.810	2.440	48.80

As a modification, therefore, the chalk lined crucible must here also be left out of consideration.

The reason that the results with the Winkler method vary so much is that the presence of copper adds a new difficulty to the assay. This can be seen from the tabulated results obtained in reducing cupric oxide for the tin assays carried out above.

In all the assays, precipitated chemically pure cupric oxide was used. If reduced completely, 5 grms. of cupric oxide ought to give 3.993 grms. of copper. In the naked crucible we obtain as an average 3.801 grms. and a discrepancy of 0.055 gm. between the highest and lowest results, which, if expressed in percentage, gives 1.1 per cent difference. In the chalk-lined crucible there is a better output in copper; if extra reducing agents be added, a still better result is obtained, even in the naked crucible, but not a correspondingly better reduction of stannic oxide. It would seem, therefore, that the amount of tin reduced will vary according to the amount of copper carried off in the slag.

TABLE XX.

Grms. of copper resulting in naked crucible with regular charge.	Grms. of copper resulting in naked crucible with regular charge and 1 gm. charcoal.	Grms. of copper resulting in chalk- lined crucible with regular charge.
3.825	3.920	3.815
3.820	—	3.810
3.805	—	—
3.785	—	—
3.770	—	—
Aver. 3.801	3.920	3.8125

In the assays with potassium cyanide it was seen that the presence of sulphates had a very bad effect on the result. As copper has a very great affinity for sulphur, the results of this bronze assay may also have been influenced by it. Several assays were made, omitting the salt and increasing the amount of potassium carbonate. The weight of the copper buttons was slightly higher, e.g., 3.850 grms.; but the reduction of the tin was very imperfect, as it did not all alloy with the copper and collected in one button of bronze; prills of bright malleable tin were found in the slag, showing that, to obtain a slag of sufficient fluidity for all reduced metal to collect in one button, the addition of salt is necessary. By reference to the German assay it will be seen that the presence of salt containing sulphates does not produce the same bad effect on tin as in the cyanide assay.

The Winkler method is given in a modified way by Ricketts:—"ore, 10 grms.; cupric oxide, 10 grms.; black flux substitute, 30 grms.; argol, 2 grms.; borax glass, 5 grms.—are well mixed, charged in a chalk-lined crucible, a salt cover and charcoal are added, and the charge heated gradually to a white heat for an hour. He advises separating tin and copper in the wet way. In this modified method, it will be seen that an additional reducing agent, argol, has been added, and that flux and ore are intimately mixed. Winkler makes a point of not mixing ore and flux, as he wishes to avoid the strong boiling of the charge, whereby particles of alloy might adhere to the sides of the crucible and escape being collected in the button.

* "Notes on Assaying," 1886, p. 89; quoting from Mitchell, "Manual of Assaying," p. 411 (probably fourth edition, as it has been omitted in the fifth edition of 1891).

Three bronze assays were carried out, and one copper assay, giving the following results:—

TABLE XXI.

No. of assay.	Resulting bronze. Grms.	Resulting copper. Grms.	Resulting tin.	
			Grms.	Per cent.
108.	13.685	7.360	6.325	63.25
109.	13.660	7.360	6.300	63.00
110.	13.630	7.360	6.270	62.70
Average ..	13.658	7.360	6.293	62.98

They show no advantage over Winkler's original method. Less tin is recovered, and more copper is scorified, and a treatment of the alloy in the wet way would be apparently a loss of time.

(To be continued).

CORRESPONDENCE.

THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—We shall be obliged if you will allow us to make the following statements in reference to the innuendoes contained in a letter in your last issue.

Our circular is, in both type and paper, totally unlike any document sent out by the Chemical Society to the Fellows, and the statement to the contrary is utterly without foundation, even though it comes from a former member of the council.

Of the hundreds of Fellows who have signed our circular thirty-eight returned them to the Chemical Society. These copies have been handed to us, and we have no reason to believe that any have been withheld.

We regret that anyone, more especially a former member of the council, should have such a poor opinion of the intellectual and moral status of the Fellows of the Society as to assume they would give their written assent to views, when promulgated by the council, which they could not assent to when promulgated by others.

Were it not that we must treat this assumption on the same basis as the rest of the letter, we think it would have been the strongest possible argument in defence of our present policy, which is to keep out of the Society those who are intellectually, or morally, unworthy of the Fellowship.—We are, &c.,

FREDERICK J. LLOYD.
FRANK L. TEED.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 18, November 3, 1890.

Action of Borax in Alkaline Developing Baths.—P. Mercier.—Sodium borate is generally considered as retarding the development, yet, as it presents an alkaline reaction, it ought to act solely as an accelerator. The explanation of this apparent anomaly may be found in a research by M. Aug. Lambert, published in the *Comptes Rendus*, and on the action of borax upon the polyatomic alcohols and phenols, and especially upon pyrogallol, hydroquinone, and pyrocatechin. It appears that boric acid combines with the primary polyatomic alcohols and

certain polyatomic phenols to give rise to certain boron-conjugated acids. Thus, borax added in small quantities to pyrogallol converts it into a true acid which reddens litmus. It is the same with tannin and pyrocatechin, so that with these substances the addition of an alkaline borate is equivalent to the addition of an acid, the salt in this case causing retardation. But this reaction is not produced with the isomers of pyrocatechin, i.e., hydroquinone and resorcin. Neither is it produced with the ether developing agents now in use. Here borax does not give rise to any acid, and acts merely by its alkalinity.

On the Affinities of Iodine in the Dissolved State.—Henri Gautier and G. Charpy.—Solutions of iodine in different liquids present a continuous series of colours from violet to brown, and to these different colours there seem to correspond different molecular condensations. The question arose if these different conditions did not introduce a modification in the chemical action of iodine. After various trials, the authors have succeeded in finding a reaction which shows a decided difference between the solutions. On agitating pure mercury with any solution of iodine, there is always formed a green precipitate of mercurous iodide; but if the mercury contains small quantities of another metal, the iodine combines with this latter in variable proportions, according to the nature of the solvent. The phenomenon is particularly distinct with lead amalgam, the yellow colour of lead iodide enabling us to follow the course of the reaction. A brown solution of iodine (in alcohol, ether, or acetone), if agitated with lead amalgam gives a yellow precipitate of lead iodide as long as traces of this metal exist in the mercury. When the precipitate takes a green tint, the mercury which remains is completely pure. On the contrary, a violet solution (in carbon disulphide, chloroform) gives, under the same conditions, a green precipitate analogous to that yielded by pure mercury. On operating with a great number of solvents, we may obtain a series of colours ranging continuously from yellow to green. The order in which we arrange the solvents is the same as that obtained by classing them according to the colour of the solutions of iodine. It appears thus that the violet solutions of iodine, which contain this body in a more simple molecular state, tend to form mercurous iodide at first.

On the γ -Cyanacetoacetic Ethers, and the Corresponding Chloroimide Ethers.—A. Haller and A. Held.—This memoir does not admit of useful abstraction.

Researches on the Conditions of the Progression of the Isopropylamines. Limit to the Progression and Development of Propylene.—H. and A. Malbot.—It is found that isopropyl chloride deviates from isopropyl iodide and approximates the orthopropyl, isobutyl, and isoamyl chlorides, which furnish free amines. There is this essential difference, that we easily obtain triorthopropylamine, tri-isobutylamine, tri-isoamylamine, but we cannot go beyond di-isopropylamine.

The Moulds of Copper and Bronze.—Raphael Dubois.—Many phenomena formerly attributed to chemical, physical, and mechanical agencies are now, thanks to the more profound study of the lower organisms, referred to the domain of biology. Numerous observations have proved that the lower beings may be developed in media formerly considered absolutely unfit for any vital manifestation. The author has recently observed in concentrated solutions of copper sulphate, neutralised with ammonia, and serving for the immersion of the gelatinous plates used in photographic engraving, whitish flocks of mycelium, presenting great analogies with those of *Penicillium* and *Aspergillus*. These mycelia are rapidly developed and fructify in Raulin's liquid, whilst in cupric solutions they remain in the mycelial state. If we pour upon a bronze coin, previously cleaned with nitric acid and well washed, a neutral solution of copper sulphate containing such mycelia, and place the coin under a moist

bell, the solution quickly changes colour at the points where the *mycelia* are collected. When the cupric liquid has completely evaporated, the surface of the coin is scattered over with spots of a characteristic malachite green resembling the patina of the most beautiful antique bronze. To be certain that the transformation of the copper sulphate into malachite is due to the vital action of the mould, the author sterilised the bronze coins in an autoclave, as well as a part of the liquid containing the *mycelia*. The copper sulphate then underwent no alteration, and the green tint of antique bronze was not produced at all. These facts show with what energy living beings can act upon inorganic matter, and how important it is to take account of their activity, especially among the causes of alteration of metals and in the formation of certain mineral bodies.

Moniteur Scientifique, Quasneville.

Series 4, Vol. iv., Part 1.

Action of Mineral Acids in Saccharification by Means of Malt, and in the Fermentation of Starchy Matters.—Dr. J. Effront.—This bulky treatise is quite incapable of useful abstraction.

Researches on the Condensation of the Carburetted Gases under the Influence of the Electric Effluve.—P. Schützenberger.—In this memoir, which is not completed, the author examines the condensation of carbon monoxide and the composition of the supposed carbon suboxide, C_4O_3 .

The Specific Gravity of Resin Oils and of Oils of Turpentine.—Adolphe Renard.—These oils are generally sold with a statement of their spec. gravity at +15. The author determines the correction to be made for higher or lower temperatures.

Detection of Olive Kernels in Pepper.—M. Pabst.—The author recommends for the detection of this fraud a test paper which has been saturated with dimethylparaphenylenediamine, as proposed by Wurster for detecting mechanical wood paste in paper, or thalline which is used in vegetable histology for colouring woody tissues. The paper is laid on a watch-glass, moistened with water, and dusted over with the suspected pepper; particles of the olive kernels are instantly coloured red, whilst pepper retains its ordinary colour. For preparing this reagent, the author mixes 10 grms. of commercial dimethylaniline with 20 grms. pure concentrated hydrochloric acid. He then adds 100 grms. of powdered ice, and then by degrees, whilst stirring, a solution of 7 grms. sodium nitrite in 100 c.c. of water. The reaction is let go on for half an hour. He adds, then, 30 to 40 grms. of hydrochloric acid and 20 grms. of tin-foil and allows the reduction to continue for an hour, and then precipitates the tin by means of granulated zinc. The liquid is decanted through a filter, then neutralised with potassium or sodium carbonate until a permanent turbidity is produced, which is re-dissolved by means of a few drops of acetic acid. Ten grms. of concentrated sodium bisulphite are added, and the whole is made up to 12 litres with water. The same reagent shows the presence of ground wood, nut-shells, &c. Thalline sulphate dissolved in 200 parts of water colours the olive kernels a very fine orange, which is produced more slowly than the red of the former test; and, further, this solution does not keep well.

Action of Carbon Disulphide upon certain Azocompounds and upon the Hydrazones.—P. Jacobson and V. Schene.—From the *Berichte Deutsch. Chem. Gesell.*

Green Ultramarine.—Dr. J. Szilasi (*Hungarian Academy of Sciences*).—The author considers it proved that green ultramarine is a definite chemical compound having a constant composition. This does not imply that all the green ultramarines answer to the same formula. It is known that there are several blue ultramarines having different compositions; some, e.g., poorer and

others richer in silica. Green ultramarine may also present different compositions, which are constant for each kind.

Researches on Narcotine.—W. Roser.—From *Liebigs Annalen*.

New Process for Preparing Phenacetine.—J. Riedel (*Archiv der Pharmacie*).—The author's process permits of the complete conversion of phenol into phenacetine. Paramidophenetol, under the influence of sodium nitrite and hydrochloric acid, is first transformed into ethoxyparadiazobenzol chloride. The solution of the latter, treated with phenol and an aqueous solution of sodium carbonate, yields a yellow amorphous precipitate of monoethylated diparadioxyazobenzene. This is purified by solution in a weak solution of sodium carbonate, from which it is precipitated with dilute hydrochloric acid. After purification it is dissolved in alcohol, caustic soda is added, and then ethyl bromide, and the whole is heated at 150° under pressure. The group OH of the second phenolic residue is transformed into the group OC_2H_5 . After having distilled off the alcohol and removed the sodium bromide formed with cold water, it is washed with dilute soda. The insoluble residue, consisting of diparadiethoxyazobenzol, is reduced by nascent hydrogen, which splits it up into two mols. of paramidophenetol, which when boiled with glacial acetic acid yields phenacetine.

Reaction of Sulphonal.—H. Wefers-Bettenk (*Chem. Repertorium*).—If 1 gm. of sulphonal is mixed with 4 gm. iron-filings, and the mixture is heated strongly in a test-tube, we perceive a smell of garlic. When cold, the contents of the tube are moistened with dilute hydrochloric acid, sulphuretted hydrogen is given off and may be recognised by means of a slip of lead-paper.

New Compounds obtained with the Alkaloids of the Cinchonas.—O. Hesse.—Prof. Hesse adds to a hot solution of the acid quinine sulphate an equivalent quantity of phenol. On cooling, there separates out an oily mass, above which there are formed fine white needles, $C_{20}H_{24}N_2O_2 \cdot SO_3 \cdot C_6H_5O + 3H_2O$. By simple re-crystallisation, a basic salt is obtained. All the compounds obtained from the phenols and the acid sulphates of quinine, hydroquinine, cinchonidine, and hydrocinchonidine behave in the same manner.

Analysis of Metallic Tungsten, of Ferro-Tungstens, and Tungsten-Steels; Ferro-Chromes and Chrome-Steels; with New Methods for Opening up these Metals.—Alfred Ziegler (*Dingler's Journal*).—The bulk of this paper will be inserted at the first opportunity.

Industrial Analysis of Wolframite.—B. Selik (*Chemiker Zeitung*).—The substance of this paper has been already inserted.

Observations on the Determination of Phosphoric Acid in Thomas Slags, and on certain Varieties of Tetrahydrated Ferric Phosphates.—G. Arth.—Already inserted.

Zeitschrift für Analytische Chemie.
Vol. xxix., No. 2.

On a New Catalytic Phenomenon and on the Dimorphism of Baryta.—Dr. G. Brugelmann.—If BaO is prepared from the hydrate in vessels of clay or of graphite, the oxide is left in needles, probably hexagonal, of the specific gravity 5.32. If BaO is obtained from the hydrate, but in a platinum vessel, the resulting oxide is regular and has the specific gravity 5.74, apparently in consequence of the catalytic action of the metal. BaO is obtained by the ignition of the nitrate in regular cubes of specific gravity 5.72. Hence the oxide is dimorphous. The assumption that pure BaO is of a greyish-white does not agree with facts. The author has obtained it in a state of purity absolutely white.

Contributions to the Characteristics of the Alkaline Earths and of Zinc Oxide.—Dr. G. Brügelmann.—This paper will be inserted in full.

On the Detection of Small Quantities of Arsenic with the Aid of the Induction Spark-Current.—Nix von Klobulow.—This paper requires the three accompanying illustrations.

The Distinction of the Jute Fibre from Flax and Hemp.—Dr. W. Lenz.—The recognition of the jute fibre by means of its known morphological characteristics, (especially the unequal thickening of the single bast fibres) is not difficult, but it requires practice and close attention. On the contrary, the different behaviour of the above-named fibres in polarised light presents distinctions which are more readily perceptible. For executing such an examination the author heats the threads of the tissue in question according to Schulze's well-known maceration process with officinal nitric acid (?), with the addition of a trace of potassium chlorate, washes with water, heats with water containing potassa to supersaturate any acid remaining in the fibre, decants off the alkaline solution, and shakes up the residual fibres strongly with pure water. The fibres are distributed very uniformly in the water, and in this state they are placed upon a microscope slide. The liquid accompanying them is let carefully to evaporate in a horizontal position, a drop of glycerin is added, a covering-glass is put on, and the object is examined after the glycerin has thoroughly penetrated the fibre. The fibre thus prepared not merely shows the characteristic thickenings of the sides, but is suitable for examination in polarised light. If the fibres are placed under the microscope with crossed nicols (dark field), almost every fibre of flax or hemp shows an exceedingly splendid play of colour. The jute fibres, on the contrary, appear more self-coloured—bluish and yellowish—and but few fibres show colours like those of hemp, but much less splendid. It is essential that the several fibres must be really separate from each other. If they lie over or close alongside each other, bright colours will appear at the points of contact even in the case of jute.

Determinations of Starch Granules in Corn.—Z. von Milkowski.—(See p.).

Chemical Examination of Combustion Gases.—Dr. Otto Schmidt.—The author's apparatus cannot be intelligibly described without the accompanying figure.

Determination of Sulphur in Iron.—L. Blum.—The author points out two objections to the process communicated by Marcel Lucien (*Chemiker Zeitung*, xii., p. 427).

An Impurity in Commercial Barium Chloride.—L. Blum.—A sample obtained by the author reduced permanganate strongly containing apparently traces of barium peroxide or of hydrogen peroxide; impurities which falsify the results in determining manganese in presence of iron by the Volhard-Meinecke method. In examining a sample of barium chloride it will be prudent to ascertain its indifference to solution of permanganate.

Simple and Rapid Development of Pure Gases.—H. Borntrage.—The author uses a mixture of acid sodium sulphate with the acid or neutral salts containing the corresponding acid. If it is desired to obtain the gas as dry as possible without a desiccating tube, &c., the author uses a carbonic acid apparatus, fills the globe usually containing marble with solid sodium disulphate in fragments, places the corresponding salt in the lowest vessel of the apparatus, and after making the connections moistens the sodium disulphate with water. The gas liberated is dried by contact with the sodium disulphate. The process is used in chemico-legal investigation.

Cutting Thick Glass Tubing.—Dr. F. Muck.—The author calls attention to an instrument, which is here figured.

Oil of Turpentine for "Denaturing" Alcoholic Liquors.—Dr. E. Meissl.—The Neustaät oil from Vienna is recommended, as it has the specific gravity 0.861—

0.865. The Russian, French, and American oils are much too heavy.

The Separation of Barium from Strontium.—Prof. R. Fresenius.—This memoir will be inserted at the earliest opportunity.

The Removal of Melts from Platinum Crucibles.—L. L. de Koninck.—Already inserted.

The Obviation of Weighed Filters in Weighing Precipitates which have not been Ignited.—L. L. de Koninck.—The author has extended the method first proposed by Professor R. Fresenius for determining potassium as double platinum-potassium chloride. He considers the process with especial reference to the determination of ammonium, arsenic, phosphorus, and magnesium, as well as zinc and cadmium. In determining ammonium as double platinum chloride the directions of Fresenius are to be exactly followed (*Zeitschrift*, vol. xv., p. 224, and vol. xvi., p. 63), i.e., the chief portion of the precipitate is to be removed from the filter, and the latter is to be replaced in the funnel. The residue is dissolved in hot water, the solution evaporated in a weighed platinum capsule, dried, and weighed after adding the bulk of the precipitate. The determination of arsenic as magnesium pyroarsenate can be effected by separating the ammonium magnesium arseniate from the filter, and placing it in a weighed crucible. The residue adhering to the filter is dissolved in a little dilute nitric acid, washed out with a minimum of water, and this liquid evaporated down in the crucible, which is then gradually heated to redness. In this manner, magnesium pyroarsenate is obtained snow-white, as the reduction of the arsenic acid is prevented by the ammonium nitrate. In a similar manner the precipitate of ammonium-magnesium phosphate may be treated in determining phosphorus or magnesium, and is always obtained white at once. The author is of opinion that the frequent blackening of magnesium pyrophosphate is due not to particles of carbon derived from the filter, but to organic bases present in commercial ammonia and in its salts. In determining cadmium and zinc by igniting the carbonates, Koninck separates the precipitate from the filter, extracts the latter with a few drops of nitric acid, washes out with water, evaporates down the solution in the crucible, and then adds the precipitate and ignites.

Quantitative Separation of Arsenic and Antimony.—O. Koehler.—H. Rose, in his *Handbuch der Analyt. Chemie* (6th edition, ii., p. 423), mentions a separation of antimony from arsenic by converting both into sulphides by precipitation with sulphuretted hydrogen, and treating the sulphides with strong hydrochloric acid, when antimony trisulphide is dissolved whilst arsenic trisulphide remains undissolved. Rose mentions that the separation is not quantitative, as a little of the arsenic trisulphide passes into solution along with the corresponding antimony compound. O. Koehler (*Archiv. d. Pharmacie*) confirms Rose's statements, but finds that a quantitative separation may be effected as follows:—20 c.c. of solution of antimony trichloride were mixed with 45 c.c. concentrated hydrochloric acid, and 5 c.c. of a solution of arsenious acid. The mixture was then heated almost to boiling, and sulphuretted hydrogen was passed in until its smell predominated after shaking. The arsenic trisulphide, clotted together in small pellets, was then filtered through a filter moistened with hydrochloric acid and washed with dilute hydrochloric acid (1:3). The precipitate, after the removal of the antimony, was oxidised with bromine-water, filtered off from residue, well washed with ammonia, and mixed with ammonia until it was decolourised. The arsenic was finally determined as ammonium magnesium arseniate.

The Use of Calcium Saccharate in place of Potassa for Absorbing Carbonic Acid.—Boner.—(*Chemiker Zeitung*). The saccharate has the defects of frothing strongly, and obstructing the narrow parts of the absorption apparatus.

On Drying the Hydracids with Phosphoric Anhydride.—G. H. Bailly and G. J. Fowler.—From the *Journal of the Chemical Society*.

Determination of Carbon in Graphite.—J. Widmer.—According to Cross and Bevan the carbon of cellulose and other organic matter is not completely oxidised to carbon dioxide by the treatment with chromic and sulphuric acids proposed by Rogers and Brunner, but is in part converted only into carbon monoxide. The author finds that this objection is not unfounded. If an acid is used made up of 2 parts by volume of sulphuric acid, and 1 part water, by weight, there was obtained only 89.18 per cent carbon instead of 94.06. Even with the most concentrated sulphuric acid carbon monoxide is still formed.

Glass for Drying and Weighing Filters.—C. Reinhardt (*Zeitschrift Angewandte Chemie*).—This note is useless without the accompanying figure.

Arrangement for Drawing off Vapours.—Cl. Winckler (*Berichte Deutsch. Chem. Gesell.*).—Requires the three accompanying figures.

Apparatus for Fractionated Distillation under reduced Pressure.—A number of devices taken from the *Berichte*, the *Chemiker Zeitung*, the *Journal of the Chemical Society*, and the *American Chemical Journal*, and accompanied by figures.

Several Laboratory Apparatus.—P. N. Raikow (*Chemiker Zeitung*).—These comprise (1) an apparatus for filtering liquids and washing precipitates *in vacuo*, or in a specific atmosphere. E. Loew (*Chemiker Zeitung*) proposes an apparatus for the same purpose. (2) An arrangement for rapid filtration, especially for amorphous precipitates. (3) A syphon for the continuous removal of an upper stratum of liquid.

An Acid-proof Exsiccator.—E. von Boyen (*Chemiker Zeitung*).—The author uses a cylindrical vaseline bath into which is introduced from above a support for the objects to be dried along with the cover.

An Apparatus for Determining the Specific Gravity of Platinum at 100°.—L. Weinstein (*Chemiker Zeitung*).—For an account of the arrangement we must refer to the original.

Safety Arrangements to Prevent Gas-Flames from Striking Back.—G. Spitz and P. N. Raikow (*Chemiker Zeitung*).

Titration of Hot Liquids.—L. L. de Koninck (*Zeit. Angewandte Chemie*).—The author uses an exit tube of the shape , so that the burette is not over, but at one side, of the hot liquid. This obviates the heating and expansion of the standard solution and the clouding of the burette.

Apparatus for Titration.—Modified burettes have been proposed by O. Kröfner (*Chemiker Zeitung*), V. Höbbling (*Zeitschrift*), Oppermann (*Chemische Industrie*).

Burette Float.—N. Wolff (*Chemiker Zeitung*) proposes small discs of paraffin of slightly less diameter than the burette and about 2 m.m. in thickness. A layer of paraffin of the required thickness is made by melting in hot water. When the cake is nearly cold it is laid upon paste board and discs of the proper diameter are cut out with the cork-borers.

Polar Contacts in Eudiometers.—C. E. Munroe (from the *Journal of Analytical Chemistry*).

Development of Chlorine for Analytical Purposes.—L. L. de Koninck (*Zeit. Angew. Chemie*).—The author recommends the action of gaseous hydrochloric acid upon granulated pyrolusite. The latter is placed in a cylinder, through which a current of hydrochloric acid streams, and the gas given off is then passed through a layer of calcium chloride and a sulphuric acid washing-bottle.

The Use of Normal Ammonia.—R. Rempel (*Zeit. Angew. Chemie*).—The author recommends that ammoniacal solutions for volumetry should never be stronger

than semi-normal. The ammoniacal solution should be let drop from a burette into the acid contained in a suitable flask. The ammoniacal liquid should be well shaken up before use. It should be kept in well-stoppered bottles and should be introduced into the burette without the use of long flexible tubes. If these regulations are carefully followed the semi-normal ammoniacal solutions will be found equal in accuracy to potassa and soda-lyes, and at the same time easier to prepare and manage.

On Sodium Carbonate.—R. Kissling.—The author has studied the behaviour of sodium carbonate when heated. From these experiments it appears that all the "semi-combined" carbonic acid is expelled at 120–130°. At 400° the residue loses some carbonic acid, and on fusion there is a decided formation of sodium oxide. Hence it is recommended that sodium carbonate to be used for standardising acids should not be heated over a direct flame, but should be kept for some time in the drying-closet at 150°. Kissling has also examined Dobbin's process for detecting caustic soda in presence of sodium carbonate. Dobbin has shown that mercuric potassium iodide gives the well-known yellow colour only in presence of caustic alkali, whilst an alkaline carbonate has no effect. This reaction can be used for the quantitative determination of caustic soda in presence of sodium carbonate by comparing the intensity of the colour with known standards. Kissling states that a quantitative determination of caustic alkali may also be based upon the fact that a mercuric potassium iodide solution mixed with ammonium chloride gives a permanent precipitate only if there is present a quantity of caustic alkali equivalent to the ammonium chloride.

Preparing the Iron Solution for Standardising Permanganate.—R. Jahoda (*Zeit. Angew. Chemie*).—A modification of the process of R. Fresenius. The flask for dissolving the iron, after receiving iron, a granule of sodium bicarbonate, and the necessary acid, is closed with a stopper which admits a glass tube bent twice at a right angle. The other end of the tube dips into a solution of sodium bicarbonate. When the solution cools at the end of the process a little of the bicarbonate solution is sucked back, and on coming in contact with the acid it evolves carbonic acid and prevents any further re-flux.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Liquorice.—Can anyone inform the writer where he can obtain any information on the adulterants and analysis of liquorice, or preparations of liquorice?—B. S. ROWNREE.

Artificial Musk.—I shall be greatly obliged to any of your readers who can inform me, through your columns, where I can obtain a sample of the artificial musk which is reported in the *CHEMICAL NEWS* (vol. lxi., p. 249) to have been discovered by A. Baur, and the patent of which has been sold to certain perfumers at Mulhouse.—M.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 1st.—Society of Chemical Industry, 8. "The Electrical Treatment of Sewage," Mr. W. Webster.
— Royal Institution, 5. General Monthly Meeting.
— Society of Arts, 8 (Cantor Lectures), "Gaseous Illuminants," by Prof. Vivian B. Lewes.
— Medical, 8.30.
TUESDAY, 2nd.—Institute of Civil Engineers, 8.
— Pathological, 8.30.
WEDNESDAY, 3rd.—Society of Arts, 8. "The Chicago Exhibition, 1893," by James Dredge, Member of Council.
THURSDAY, 4th.—Chemical, 8. Ballot for the Election of Fellows.
— "On the Volumetric Estimation of Tellurium," by Dr. Brauner.
FRIDAY, 5th.—Geologists' Association, 8.

ERRATUM.—P. 259, col. 2, line 19, for "square" read "square roots."

THE CHEMICAL NEWS.

VOL. LXII. No. 1619.

ON THE LAW OF DIFFUSION OF LIQUIDS.

By H. M. VERNON.

THOUGH Graham (*Phil. Trans.*, 1850, 1 and 805) made a very large number of careful and exact experiments on the diffusion of aqueous solutions of various salts for various periods of time, at different temperatures and at varying concentrations, yet no general law as to the relations between the salts and the amounts of them diffused under similar conditions as to time, temperature, and concentration, was shown to exist. Graham found that several series of isomorphous salts diffused at approximately equal rates, and he endeavoured to show that the rates of diffusion of several of the different groups were to one another as the square roots of simple numbers, such as $\sqrt{2}$ to $\sqrt{3}$, for he argued that, as with gases the rate of diffusion varied inversely as the square roots of their densities, some similar kind of relation should also obtain for the diffusion of liquids. Though the experimental results correspond in a few instances with numbers obtained empirically as above, yet it was probably due to chance, as there is no apparent reason why such in reality complex relations should exist. The object of this paper is to show that in all probability there exists a general law for the diffusion of aqueous solutions of salts.

From the kinetic theory of molecular motion, it follows that solutions of the same density should have equal rates of diffusion, supposing no combination takes place between the solvent and the body dissolved in it. In a series of salts arranged regularly according to the densities of their solutions, we should therefore expect that the amounts of salts diffused varied regularly from one end of the series to the other.

Graham considers in his experiments it is a remarkable fact that the quantities of various isomorphous salts diffused should be equal, and should not be to one another in proportion to their molecular weight. There is really nothing remarkable in the fact, as it must be remembered that equal and not molecular weights of the salts were taken in the first case, and that the solutions therefore contained varying numbers of molecules, just as the amounts of salts diffused if expressed in molecular weights would be variable. In all the instances tried in moderately dilute solutions, Graham has shown that the amount of substance diffused is directly proportional to the concentration of the solution, so therefore the rule he gives that several groups of isomorphous salts diffuse in equal quantities, may be better expressed by saying that equal members of molecules of the salts of several groups of isomorphous bodies diffuse in the same time.

In Graham's experiments, the times during which diffusion took place were arranged so as to give as nearly as possible equal amounts of diffusate in all cases, he then endeavouring to find numerical relations between the times thus obtained. As, however, it was also found that the amount of salt diffused was proportional to the time of diffusion, it is possible to calculate all his results to a constant time. In his experiments the times varied from 4.04 days to 16.16 days. In the tables given below all the results are calculated out to a constant period of eight days.

Though the amount of any salt diffused should depend solely upon the density of the solution and the molecular weight of the salt, supposing no combination between it and the liquid took place, yet we could not expect such a relation to hold with water for a solvent, as in all prob-

ability some combination takes place between the molecules of salt and the molecules of water. It is probable, however, that the modifying action thus introduced is not very great.

We must now examine Graham's results and see if they bear out our theoretical deductions. The values given are all for 1 per cent solutions. Determinations were made in most cases for 2, 4, and 8 per cent solutions, but it appeared that the values for more concentrated solutions were not so regular as for dilute solutions, but were affected by internal molecular forces just as gases at pressures considerably removed from that of their condensation obey Mariotte's law more exactly than at pressures near to it.

In the following table all the diffusions were performed at a temperature of about 16° C. The rate of diffusion greatly increases with increase of temperature, but as the rate of increase is not known in most cases, the values have not been calculated to a constant temperature, but have been left unaltered.

Substance.	Temperature.	Density.	Diffused from 1 p.c. solution in 8 days.
Ammonium bicarbonate ..	20.1°C	1.0049	6.84
Potassium chloride ..	16.7	1.00697	9.37
Sodium chloride ..	17.4	1.0076	7.18
Potassium bromide ..	15.4	1.0077	8.77
Potassium thiosulphate ..	15.3	1.0078	6.14
Potassium chromate ..	15.5	1.0078	6.14
Sodium bromide ..	15.4	1.008	6.85
Sodium iodide ..	15.4	1.0081	6.97
Potassium sulphate ..	15.7	1.00839	6.09
Sodium thiosulphate ..	15.4	1.0084	4.73
Potassium sulphite ..	15.3	1.0084	5.61
Sodium sulphate ..	15.5	1.0094	5.01
Sodium chromate ..	15.5	1.00953	5.04
Potassium carbonate ..	17.6	1.00957	6.09
Sodium sulphite ..	15.3	1.0106	4.79
Magnesium sulphate ..	18.5	1.0108	3.67
Sodium carbonate ..	17.4	1.0112	4.88
Aluminium sulphate ..	18.5	1.0116	2.70
Zinc sulphate ..	18.5	1.0183	3.30

In this table the salts are arranged in order of the densities of their solutions. We see that the diffusion values decrease more or less regularly with increase of density of the solutions. There are, however, several marked exceptions. Graham found that if two salts were allowed to diffuse, the amount diffused was not so great as if each salt had been allowed to diffuse in a separate solution, but that each salt to a certain extent retarded the diffusion of the other. In this table the value for ammonium bicarbonate is less than the normal, and so probably the molecules of this salt when in solution have undergone dissociation. This view is strengthened in

Substance.	Temperature.	Density.	Diffused from 1 p.c. solution in 8 days.
Ammonium chloride ..	11.7°C	1.0036	8.38
Hydrogen sulphate ..	9.8	1.0065	6.95
Sodium nitrate ..	11.7	1.0070	6.30
Magnesium nitrate ..	10.4	1.0073	4.54
Potassium iodide ..	11.9	1.0075	7.87
Copper nitrate ..	10.4	1.0075	4.50
Strontium nitrate ..	10.8	1.0077	4.75
Magnesium chloride ..	10.3	1.0077	4.31
Calcium nitrate ..	10.8	1.0081	4.48
Barium nitrate ..	10.8	1.0083	4.71
Manganese chloride ..	10.4	1.0085	4.72
Silver nitrate ..	10.8	1.0089	6.31
Calcium chloride ..	10.5	1.0090	4.55
Zinc chloride ..	10.5	1.0091	4.40
Copper chloride ..	10.3	1.0093	4.24
Barium chloride ..	10.5	1.0095	5.25

that this salt is known to be exceedingly unstable. The same also applies to the salts potassium and sodium thio-sulphate, which also show abnormally low values. As we continue down the table there appear no other very great irregularities till we get to aluminium sulphate, the low value of which also seems to indicate partial dissociation when in solution.

In this table the diffusions were performed at a temperature of about 10°C. It will be noticed that the diffusion values are not so regular as before, and also that they do not exhibit much decrease as the density of the solutions increase. This is partly accounted for by the fact that the densities themselves do not exhibit so much variation, they varying from 1.0036—1.0095, while in the previous table they varied from 1.0049—1.0193.

The most marked exceptions in this table are magnesium nitrate with a value below the normal, and potassium iodide, silver nitrate, and barium chloride, the values of which are considerably above the average. Why these salts should have such high values it is impossible to say; it may be that some errors have been committed in the determinations of the densities of their solutions.

From the above diffusion experiments we see that several of the salts in solution have undergone partial dissociation. If, however, diffusion values had been taken at higher temperatures, we should expect the dissociation to be still greater, and so more marked deviations from the normal values would be obtained. Graham has determined the diffusion values for several salts at two different temperatures. The mean rates of increase of diffusion for each degree from about 10°C. to 16°C. are here given—

Barium nitrate .. 0.140	Hydrochloric acid .. 0.311
Calcium chloride 0.196	Sulphuric acid..... 0.367
Sodium nitrate .. 0.268	Silver nitrate 0.410

As in most cases the density increases regularly with increase of temperature, so we should expect the increased rates of diffusion to be much more similar than we find them here; hence these results strengthen the supposition of dissociation taking place. It might be said that if dissociation did take place, then one product would diffuse more rapidly than the other, and so the diffuseate would contain some free acid, acids being known to diffuse faster than bases. It is possible that such was the case, but as Graham estimated the diffused salts by evaporating the solutions to dryness and weighing, the free acids would volatilise and so would not appear in the result. If extremely dilute solutions were used, the method of diffusion might be considered to afford a very good proof as to whether all salts in solution undergo dissociation, as has been recently affirmed by Van't Hoff from theoretical deductions.

In the above tables the diffusion values for HCl, HNO₃, NaOH, and KOH have been left out. They were very much greater than the normal, and appeared to follow some quite different rule than the rest of the substances experimented on.

We may therefore conclude that Graham's experiments show that solutions of the same density have equal rates of diffusion, or that with solutions of varying density the rate of diffusion decreases regularly with increase in the density of the solutions. If the diffusion of salts in solutions be looked upon as quite analogous to the diffusion of gases, it is difficult to understand why the densities of the salt solutions should have any effect at all on the diffusion values. It is therefore probable that the cases are not strictly analogous, but that in liquid diffusion the molecules move in much larger masses or aggregations, and so the actual question of mass comes in. In fact, we may consider the diffusion of salt solutions to be more analogous to the diffusion of gases at temperatures and pressures near to their condensation points than to the diffusion of "perfect" gases.

THE DRY ASSAY OF TIN ORES.*

PART II.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Continued from p. 271).

5. *Iron Assays.*—Two sets of assays were made, the one recommended by Ricketts,† for tin ores containing silica only, the other by Mitchell,‡ for ores containing silica, and for tin slags.

The method is based on the fact discovered by Berthier,§ and already alluded to, namely, that iron completely precipitates tin from its combination with silica as metal, if added in sufficient quantity; if not, the stannic oxide is reduced only to stannous oxide, the iron itself being at the same time oxidised to ferrous oxide. Any excess of iron will alloy with the resulting metallic tin.

(1.) Ricketts gives the formula:—Ore, 10 grms.; hæmatite, 3 to 8 grms.; potassium cyanide, 40 grms.; and says:—"Mix and charge in a charcoal-lined crucible, cover with cyanide, and then with charcoal, lute and heat strongly from one half to one hour, remove, tap carefully, cool, and break. If the tin be in small buttons, collect by washing with water to separate the charcoal, dry, and weigh. Treat the button as an alloy of tin and iron."

The result of the experiment was a porous, greyish-black slag, through which small buttons of alloy were finely disseminated, and in the bottom of the crucible a button. Button and larger prills were picked out, the crucible lining crushed, the pulp screened, the scales and the siftings obtained from panning the pulp weighed with button and larger prills. The weights of the alloys were 8.355 and 8.320 grms., which shows a close agreement, if the amount of iron is the same in both cases. This assay was not further pursued, as there are more simple methods for obtaining accurate results. The silica of ores "containing silica only" can be treated in a much more simple way. It can be removed by washing, and the pure black tin assayed with potassium cyanide, or, if too great a loss of cassiterite is feared, the silica can be removed by hydrofluoric acid, and the resulting pure black tin then assayed. This method of assay has therefore little value for the assayer, except that it substantiates an interesting fact, namely, that iron carries down all the tin.

(2.) Mitchell|| mixes 400 grains of ore with 200 grains of ferric oxide, 100 grains of fluor-spar, and 100 grains of charcoal powder, charges the mixture in a covered crucible, keeps it at a dull red heat for half an hour, and then at a white heat for another half-hour.

In the experiments the above quantities were reduced to a basis of 10 grms. of ore. These resulted in a hard, rough, bluish-black shell, with bronze coloured stains. The inside was filled with fine charcoal, no button or any prills being visible. Apparently the ore and the hæmatite had united to form a slag. The method was not further investigated. If tin slags are to be assayed, it is a simple matter to decompose the finely pulverised slag with sodium or potassium disulphate, and then treat with acidulated water, when stannic oxide and silica will be left. The tin in this mixture can then be readily determined.

(3.) One more experiment remains to be mentioned here, i.e., the fusing of black tin with potassium ferrocyanide and potassium cyanide. Bloxam¶ states that by using this reagent all the tin can be obtained as an alloy. The idea that led to the experiments was, that if a weighed amount of dried ferrocyanide were fused with the

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 3.

† "Notes on Assaying," 1886, p. 89.

‡ "Manual of Assaying," 1881, p. 483.

§ "Traité des Essais," 1847, vol. ii., pp. 459, 460, 484.

|| "Manual of Assaying," 1881, p. 484.

¶ *Journal of the Chemical Society*, New Series, vol. iii., 1865.

ore, the buttons obtained from a number of assays would all have the same weight. If all the iron set free by the decomposition of the ferrocyanide alloyed with the tin, the percentage of tin could be readily calculated.

In the experiments, 5 grms. of ore were mixed with 5 grms. of dried potassium ferrocyanide and 5 grms. of potassium cyanide. For the bottom of the crucible, and for the cover, 5 grms. of potassium cyanide were reserved. The results of the experiments were negative. The alloy was partly disseminated through the lower grey slag, which was porous and tough, and had partly collected in a button. The weights of several 5-grm. assays did not agree within 1 grm., showing that all the iron of the ferrocyanide had not united with the tin, but that part had remained suspended in the lower slag.

Class B.

The second group of assays comprises the Cornish methods, which are only for determining the tin obtained by treating the ores on a large scale. That the results of such assays must be wrong is conceded. How closely they may agree when repeated in the same way by the same person is not stated.

6. Mitchell* and Ricketts† give the following method "for pure tin oxide":—400 grains (Mitchell), or 10 grms. (Ricketts) are placed in a charcoal-lined crucible, to which a cover is luted. The crucible is heated gradually for twenty-five minutes, finishing the operation at a white heat.

For the experiments, 25 grms. of ore were treated as described. There resulted, in the bottom of the crucible, a dull button of tin, while on the walls and bottom were numberless bright prills of tin. Button and prills were free from iron. The charcoal lining was pulverised and made to pass a 60-mesh sieve. The button, the scales on the sieve, and the siftings resulting from the pulp that had been panned were weighed together. The weights of two assays were:—

18.120 grms. = 72.5 per cent tin.
16.150 " = 64.6 " "

The chemical analysis shows only 67.84 per cent of tin. The reason for this strange result is to be sought in the panning of the fine pulp. When all the charcoal has been washed off there remains in the pan a heavy, black residue. It is almost impossible to see what part of this is fine tin and what heavy slag, as they scarcely differ in appearance. It is certain that with the result 72.5 per cent slag still remained with the tin, and it is not at all sure that it was all removed with the result 64.7 per cent. Perhaps after long acquaintance with uniform ores some approximately reliable estimates might be obtained, but as far as exact results go the method appears to the writer a very doubtful one.

7. Another method is given by Mitchell‡:—2 ounces of ore are mixed with a small quantity of culm and projected into a red-hot, naked crucible; some fluor-spar is added if necessary, and after a quarter of an hour's fusion the tin is poured. The prills in the slag are recovered by pounding and vanning.

In the experiments, 50 grms. of ore were mixed with 12 grms. of finely pulverised anthracite, shot into the red-hot crucible and heated for half an hour, a little fluor-spar having been added. No fusion was apparent. The crucible was removed, and broken when cold. It contained a black, porous, fritted mass, full of prills of tin, and on the bottom a button. The entire lower part of the crucible was crushed, screened, and panned, and all the recovered tin weighed together. The weights were:—

34.10 grms. = 68.20 per cent tin.
27.38 " = 54.70 " "

The same difficulty as above in separating the heavy, black slag from the fine tin causes the irregularity.

8. In connection with the Cornish methods it may be mentioned here that it has been the writer's custom, in melting out metallic tin from different grades of black tin, to mix the black tin with 5 per cent of lime, 5 per cent of fluor-spar, and 12 to 15 per cent of charcoal or anthracite, the latter requiring a higher temperature, but giving cleaner slags. With pure concentrates obtained from ore occurring in quartz no special difficulties have been encountered, so that the entire contents of a plumbago crucible weighing about 10 pounds can be readily poured. With impure concentrates the results of such fusions have always been somewhat pasty slags, and additions of lime or fluor-spar were never of much avail. The only remedy has been to add salt, which makes the slags less pasty. The main point in all these fusions is always to have the crucible nearly filled. If the first charge has begun to fuse, a second one is added. Such a fusion takes from one to two hours. Unfortunately, no records have been kept of the amount of white tin contained in the black, which would give the amounts saved.

In reviewing the preceding experiments, it is striking that so many different methods and modifications should still be recommended when a few simple ones are quite sufficient. The experiments made show clearly that there are only two methods giving entirely satisfactory results. These are the German method, as exemplified by assays Nos. 1 to 6, and the method of fusion with potassium cyanide, as from assays Nos. 35 to 38; or, still better, if sufficient material is available, Nos. 39 to 42.

In the following investigations concerning the influence the different minerals associated with the black tin have on the results of these assays, we shall see to which of the two methods the final preference is to be awarded.

(To be continued).

ON THE REMOVAL OF GOLD FROM SUSPENSION AND SOLUTION BY FUNGOID GROWTHS.*

By A. LIVERSIDGE, M.A., F.R.S., Professor of Chemistry
in the University of Sydney.

SOME examples of gold removed from solution and suspension by fungoid growths were first exhibited by the author at a meeting of the Royal Society of New South Wales in September, 1889. Since then several additional experiments have been made under known conditions and with a gold solution of known strength.

On the occasion referred to, the fungoid growths exhibited had formed in bottles of distilled water, containing very finely divided gold in suspension, which had been prepared at different times to show a class of students that, under ordinary circumstances, gold reduced from a weak solution of the chloride by means of phosphorus dissolved in ether, usually takes several years to completely precipitate and yield a clear solution.

On examining the bottles, some of which had been settling since 1881, it was found that those containing a colourless liquid were also characterised by the presence of fungoid growths, usually at the bottom of the bottles; those without fungoid growths still possessed either the ruby red or the purple colour characteristic of gold reduced by phosphorus in ether; i.e., the gold still remained in suspension.

In the case of a bottle put up on 28th November, 1884, a purple-blue growth had formed, and the solution was practically colourless; the bottle had not been opened since 1884, and had been kept in the dark for six years. On removing the stopper the odour of ether was still present.

* *Op. cit.*, p. 480.

† *Op. cit.*, p. 88.

‡ *Op. cit.*, pp. 480 and 481.

* From the *Transactions of the Australasian Association for the Advancement of Science*, Melbourne Meeting, 1890, Section B.

Under the microscope, with a low power, the growth had the appearance of a mass of matted purple-blue filaments; when dried over a spirit lamp the filaments retained their form, but lost their purple colour and acquired the metallic lustre and colour of gold.

When the growth was rubbed in a mortar it also immediately acquired the colour and lustre of gold.

Although none of the solutions free from fungoid growths were colourless, many of those with fungoid growths still possessed tints of ruby or purple, even after standing for five or six years, e.g., a solution in a bottle put up on 1st December, 1884, was, in September, 1889, still of a deep purple-red colour, with a large, purple-red, muffin-like mould at the bottom of the bottle some $3\frac{1}{4}$ inches across and $\frac{1}{2}$ of an inch thick; but by 29th May, 1890, the whole of the colour had disappeared from the liquid. The disappearance of the tint between September, 1889, and 29th May, 1890, may have been hastened by the exposure of the bottle to daylight.*

In the case of a quart bottle put up on 30th April, 1885, the solution was, in October, 1889, perfectly colourless, and the fungoid growths were of a different character, some being white and others blue-black; the white ones were floating oval bodies, about $\frac{1}{4}$ of an inch in length, with a blue-black nucleus.

(Specimens of these growths, together with microphotographs and drawings of the same, enlarged 1000 diameters, were exhibited).

The gold in the foregoing experiments was, of course, merely in suspension, having been reduced by the phosphorus in ether prior to the formation of the growth. The growth seems to have been in most instances merely instrumental in removing the gold from suspension, although such growths will reduce or precipitate the gold as well as remove it from suspension.

The growths seem to have formed much more readily in those cases where phosphorus in ether or alcohol was used, and this may have been due to the oxidation of the phosphorus to phosphoric acid, the presence of which is, of course, favourable to such growths, and the ether and alcohol may have, in part, served as food for the moulds, since there was no growth, or but very little, when other solvents for the phosphorus, such as carbon disulphide, chloroform, turpentine, and benzene were used.

On 11th October, 1889, ten confirmatory experiments under known conditions were started. Several pint bottles of distilled water were put up, and a definite quantity of the ordinary crystallised gold chloride was added to each. The gold chloride solution was made by dissolving a fifteen-grain tube of the $\text{AuCl}_3 \cdot \text{NaCl} \cdot 2\text{H}_2\text{O}$ salt in 500 c.c. of water, and 5 c.c. of this solution were added to each pint (20 fluid ozs.) of distilled water, and a small quantity of the reducing solution or agent added at the same time. The bottle was then filled up to the stopper with distilled water, and not re-opened until the time arrived for examining the growth, if any, which had formed. These bottles are not placed in the dark as in the first experiments.

Roughly speaking each bottle contained 0.01 grm. of the crystallised gold salt.

In addition to chemical reducing agents various organic ones were made use of, and as I was not in a position to obtain named fungi, I made use of certain fungoid growths, which can always be obtained in a chemical laboratory, so that the experiments can be easily repeated, and the growths used can, if necessary, be identified and named.

Amongst those used, which are all likely to be more or less pure growths, were the moulds which form spontaneously in solutions of the following:—

1. Potassium acetate.
2. Citric acid.
3. Oxalic acid.
4. Magnesium sulphate.
5. Potassium tartrate.

The mould (*Penicillium*?) from cheese and banana skins was also used. Bread and other organic bodies were also employed. All of these were found to remove the gold more or less completely from both solution and suspension, and to become stained with the ordinary blue-purple colour characteristic of gold absorbed or taken up by organic matter.

All the bottles put up prior to October, 1889, had been kept in a cool, dark room, without a window, and the door of which was seldom opened, hence the change may in these cases have gone on more slowly.

Although the fungoid growth had been observed in some of the bottles prior to October, 1889, no special attention was paid to the matter until that date, hence in the table which follows no remarks are appended before that date.

The amount of gold chloride in bottles from one to eight is unknown, but from number nine to the end of the series it is 0.01 grm. (roughly) of the crystallised double gold and sodium chloride.

Since the note was communicated to the Australian Association and pending the printing of the paper, I have been able to add observations upon the solutions up to the 28th May, 1890.

The following table shows the changes which took place in the solutions of gold chloride on the addition of various reducing substances; the first date indicates when the solution was put up and the other dates when the observations were made.

REAGENT AND RESULTS.	
Date.	No. 1.
1 12 84.	Phosphorus in Ether.
1 1 90.	Blue-purple colour. Heavy blue-black growth.
22 5 90.	Blue-purple solution. Heavy blue-black growth, one mass of which $2\frac{1}{2}$ inches long and 1 inch wide.
28 5 90.	No further change.
No. 2.	
1 12 84.	Phosphorus in Ether.
1 1 90.	Perfectly colourless solution. Blue-black growth. Photographs and sketches were made of this.
22 5 90.	Colourless solution. Blue-black voluminous growth, with some light-coloured growth.
28 5 90.	No further change.
No. 3.	
30 4 85.	Phosphorus in Ether.
1 1 90.	Quart bottle. Solution colourless. Both white and blue-black fungoid growths had formed. The white were fluffy, about $\frac{1}{4}$ of an inch through, quite different from the other growths, and possessing a blue-black nucleus or centre.
No. 4.	
30 4 85.	Phosphorus in Ether.
1 1 90.	Colourless solution. Blue-black growth.
22 5 90.	Very pale slate coloured solution. Blue-black growth, and a downy white growth streaked in places with blue-black.
28 5 90.	Solution colourless. Blue-black flocculent voluminous growth, also amoeba-like growth of very pale-blue tint.
No. 5.	
23 11 85.	Phosphorus in Ether.
1 1 90.	Deep blue solution. Voluminous blue-black growth.
22 5 90.	Purple solution. Large black growth.
28 5 90.	Purple solution. Voluminous blue-black growth.

* This observation is now added to the paper as originally read.

No. 6.

- 23 5 88. *Phosphorus in Ether.*
1 1 90.—Water tinted with dark blue. Precipitate blue-black, rather denser and not so much fungoid growth as in the others.

No. 7.

- 23 5 80. *Phosphorus in Ether.*
1 1 90.—Greenish solution. Blue-black growth.
22 5 90.—Nearly colourless solution, but of a light purple-slate colour.
28 5 90.—Pale blue solution. Blue-black growth, in loose pieces about $\frac{1}{4}$ of an inch through.

No. 8.

- 15 8 89. *Phosphorus in Ether.*
Liquid of a red-purple colour. Only a slight amount of mould, also of a purple-red colour.
28 5 90.—No further change.

No. 9.

- 11 10 89. *Phosphorus in Ether.*
14 10 89.—Nearly colourless. Slight bluish-green precipitate.
1 1 90.—Red solution. Voluminous purple-red growth.
22 5 90.—Red solution. Voluminous purple-red growth, and a few minute portions of whitish growth.
28 5 90.—Red solution. Floating voluminous purple-red growth and a compact adherent growth at bottom of bottle.

No. 10.

- 21 11 89. *Phosphorus in Ether.*
1 1 90.—Deep purple-red solution. No growth, and little sediment.
22 5 90.—Solution almost colourless, but pale slate-colour. A considerable quantity of almost black sediment.
28 5 90.—Solution practically colourless. Dense blue-black growth at bottom of bottle.

No. 11.

- 15 8 89. *Phosphorus in Ether.*
1 1 90.—Dark purple-red solution. Dark purple-red growth.
22 5 90.—No apparent alteration.
28 5 90.—Fairly deep purple solution. Bluish-black voluminous growth.

No. 12.

- Potassium Acetate Mould.*
11 10 89.—Gold reduced immediately, and the solution became of a pale blue colour in ninety minutes.
14 10 89.—Dense blue-purple precipitate. Clear colourless solution. Mould stained blue-purple.
1 1 90.—Dense thin adherent dark purple deposit in addition to mould.
22 5 90.—Deposit very deep black.
28 5 90.—Deposit very deep black. Solution very pale slate colour.

No. 13.

- Phosphorus in Benzene (C₆H₆).*
11 10 89.—Purple-blue colour. No precipitate. No growth.
1 1 90.—Purple-blue solution. No growth and no deposit.
22 5 90.—Slight deposit of a dark purple colour.
28 5 90.—Solution of a fairly deep purple colour, apparently turbid. No further deposit, and no mould or growth.

No. 14.

- Citric Acid Mould.*
11 10 89.—Pale blue colour in ninety minutes.
14 10 89.—Red purple solution. No precipitate and no growth.
1 1 90.—Pale blue solution. Indigo-blue fungoid growth.
22 5 90.—Mould almost black, one piece $\frac{1}{8}$ in. $\times$ $\frac{1}{8}$ in.
28 5 90.—Solution colourless. Deep blue-black deposit, and free lump of similar-coloured growth.

No. 15.

- Phosphorus in Alcohol.*
11 10 89.—Dirty brown colour at once.
14 10 89.—Blue-purple solution. No precipitate or growth.
1 1 90.—Pale purple-blue solution. Small quantities of bluish growth.
22 5 90.—Considerable quantity of blue-black growth.
28 5 90.—Pale tint of blue left in liquid. Thick blue-black deposit evenly covering all the bottom of the bottle.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 20th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Arthur Colefax, B.A., Ph.D., Ashgrove, Bradford, Yorkshire; Ernest F. Hooper, Elmley, Beckenham; Moses William Jones, 343, Aspen Terrace, Church, Lancashire; Stephen Newcombe Wellington, Riverdale House, Brundall, Norfolk; Thomas M. Wyatt, 20, Queen Square, W.C.; David Wilkinson, Dunedin, Otago, New Zealand.

The following were elected Fellows of the Society:—Messrs. Charles F. Branson; D. G. Clark; Charles Edwin Day; Robert Frost; Colin Gordon; Arthur R. Haslam, Ph.D.; Wallis Jenkins; John McKillop; Thomas Rhymer Marshall; William Alexander McCubbin; Thomas Parkes; Richard James Redding; Edward Cox Seaton; Frederick Smith; John Brooks Thornley; and James Mitchell Wilson.

The following papers were read:—

90. "A New Method of Determining the Specific Volumes of Liquids, and of their Saturated Vapours." By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

When a tube closed at both ends and partly filled with a liquid is raised in temperature, the liquid expands, but the apparent expansion is less than the real, for a certain amount of the substance separates and occupies the space above the liquid in the form of saturated vapour. If the density of the vapour were known, it would be possible to apply the necessary correction; but at high temperatures and pressures this is not the case. If, on the other hand, the upper part of the tube (enclosing the vapour and a portion of the liquid) be heated to a high temperature, the lower part being kept at a constant low temperature, and if, subsequently, a greater length of the tube be heated to the high temperature, there will again be expansion; but in this case the observed expansion will be greater than the real; for, in consequence of the diminution in volume of the saturated vapour, a portion of it must have condensed.

In both cases we have the same two unknown values the true volume of the liquid and the specific volume of the vapour, and from the two equations involving the experimental data, it is, therefore, possible to calculate both values.

The experimental method, based on the principles just described, is described in full in the paper. It possesses the following advantages:—It is applicable to substances such as nitrogen peroxide or bromine, which attack mercury; it is available for a very wide range of temperature and pressure, even to the critical points of many substances, the data obtained serve to determine not only the specific volume of the liquid but also that of its saturated vapour.

91. "The Molecular Condition of Metals when Alloyed with each other." By C. T. HEYCOCK and F. H. NEVILLE.

In the *Journal of the Chemical Society* for May, 1890, we showed that 1 atomic proportion of a metal when dissolved in tin produces the fall in the freezing-point that, on the theory of osmotic pressure, should be produced by one molecular proportion: we therefore concluded that when metals are dissolved in tin their molecules are monatomic. During the past summer, we have succeeded in carrying out similar experiments, using bismuth, cadmium, and lead as solvents. The method of experimenting was practically the same as for tin. We now give a brief abstract of our results. The molecular falls predicted by the theory of osmotic pressure, that is, the falls that one molecular proportion of any substance ought to produce when dissolved in 100 atomic proportions of the solvent metal, are as follows:—

Solvent bismuth, mol. fall is 2.08° C.

Solvent cadmium " " 4.5° C.

Solvent lead " " 6.5° C.

Hence, the following tables show that the atom is identical with the molecule in many cases:—

Bismuth.

	No. of experiments.	No. of atoms per 100 atoms Bi.	Mean atomic fall.
Lead ..	20	1.1—1.75	2.1
Thallium ..	2	0.3—0.9	2.07 M.
Mercury ..	4	0.3—4.3	2.04
Tin ..	4	0.16—2.2	2.03 Steady.
Palladium ..	4	0.9—2.2	2.03
Platinum ..	6	0.2—1.2	2.02 Steady.
Cadmium ..	4	1.0—4.0	2.01
Gold ..	4	0.4—1.8	1.97
Sodium ..	3	0.8—4.0	1.94 Steady.
Silver ..	3	0.7—2.5	1.91
Zinc ..	4	1.3—4.8	1.6
Copper ..	5	0.23—0.6	1.23
Arsenic ..	5	0.25—2.3	0.68 Very steady.
It is noticeable that arsenic both in bismuth and cadmium gives $\frac{1}{2}$ fall.			
Antimony ..	3	0.23—1.0	2.79 Rise.

Cadmium as a Solvent.

	No. of experiments.	No. of atoms per 100 atoms Cd.	Mean atomic fall.
Antimony ..	2	0.3—0.5	4.71 M.
Platinum ..	2	0.08—0.13	4.55
Bismuth ..	4	0.05—0.5	4.58
Tin ..	3	2.2—3.6	4.09
Tin ..	2	0.66—2.6	4.48
Sodium ..	3	0.6—1.3	4.44
Lead ..	2	0.84—1.4	4.4
Thallium ..	3	0.24—1.28	4.34 M.
Copper ..	8	0.2—2.0	3.5 No falling off.
Mercury ..	3	0.23—0.68	2.77
Zinc ..	3	0.06—1.6	2.72 No falling off.
Palladium ..	3	0.13—0.26	2.35
Potassium ..	2	0.5—0.6	2.26 M.
Gold ..	3	0.14—0.7	1.48
Arsenic ..	1	0.2	1.6

Seven out of fourteen metals appear to have monatomic molecules, the osmotic pressures ranging from 2 to more than 40 atmospheres. In the case of zinc, palladium, and mercury, there is a smaller fall even at the low pressure of 2–8 atmospheres.

Arsenic gave a fall of $\frac{1}{2}$.

Silver 1 0.05 9.33 Rise.

The dissolved substance separates from the solution as temperature falls.

	No. of experiments.	No. of atoms per 100 atoms of Sn.	Mean atomic fall.
Gold ..	4	0.33—2.7	6.45 Steady.
Palladium ..	3	0.32—1.8	6.45
Silver ..	6	0.2—1.4	6.45
Platinum ..	4	0.15—0.6	6.42
Copper ..	3	0.1—0.195	6.15
Arsenic ..	4	0.38—4.9	5.33
Magnesium ..	2	1.5	4.56
Zinc ..	3	0.2—1.2	4.43
Antimony ..	4	0.6—4.7	3.9 Steady.
Cadmium ..	2	0.6—6.1	3.62 Steady.
Mercury ..	3	0.73—6.7	3.31 $\frac{1}{2}$
Bismuth ..	6	0.23—4.6	3.02 Steady.
Tin ..	3	0.4—1.8	1.8
Sodium ..	2	6.0—9.0	1.6 $\frac{1}{2}$ Sn ₄ .

Theoretical fall = 6.5.

Of the fourteen metals dissolved in lead, it would appear that five have monatomic molecules; while mercury, bismuth, and cadmium are diatomic; the molecule of tin would seem over a long range to be tetraatomic.

92. "The Estimation of Cane-sugar." By C. O'SULLIVAN, F.R.S., and FREDERIC W. TOMPSON.

The authors describe a new method of estimating sucrose, which they claim is applicable to all solutions containing cane-sugar, including natural juices and other preparations in which the use of acids is not possible. The process is a very simple one, and it is shown, by comparing it with estimations in which invertase is used, that it is very accurate. It is based on the one used by Kjeldahl in 1881, and is as follows:—

The neutral solution containing cane-sugar is placed in a constant temperature bath at 55°. A little pressed brewer's yeast is added, and complete admixture secured by gentle stirring. At the end of four hours inversion is nearly always finished. The solution is cooled, made up to double its original bulk and filtered. During the process there is a decrease in the optical activity of the solution, and an increase in the cupric reducing power. Each of these factors is an accurate measure of the amount of cane-sugar originally present. The authors quote experiments showing that good results are thus obtained in solutions which would not admit of the use of acids.

93. "The Spectra of Blue and Yellow Chlorophyll, with some Observations on Leaf green." By W. N. HARTLEY, F.R.S.

The author refers to the numerous memoirs on chlorophyll of Stokes, Sorby, Chautard, Timiriaseff, Pringsheim, Reinke, and of Russell and Lapraik and Schunck. Having been occupied at various times during the last seven years in an investigation of the different colouring-matters described under the name of chlorophyll, he has deemed it advisable to present his results to the Society without awaiting the further development of the research. The subject-matter may be conveniently arranged under the following heads:—

- Observations on the spectrum of chlorophyll contained in living tissues.
- The spectrum of chlorophyll as seen in dried leaves.
- Mode of extracting leaf-green unchanged and separating the blue from the yellow chlorophyll.
- Measurements of the spectra of the chlorophylls.

1. Living tissues which are fresh and young, and which therefore contain the leaf-green unaltered, exhibit no trace of a band in the yellow close to D, such as is usually attributed to chlorophyll, and there is no indication of one in the green. Complete absorption, just beyond δ , extends through the ultra-violet.

2. Yellow chlorophyll has a distinct absorption-band in the red differing from that of blue chlorophyll. It has likewise a distinct fluorescence.

3. When light is concentrated on living tissues the

absorption spectrum of the green colouring-matter is soon altered.

4. Separation of blue from yellow chlorophyll. The blue chlorophyll may be extracted from minced leaves by cold absolute alcohol, and may be precipitated by addition of baryta. The yellow chlorophyll is not so precipitated, or not precipitated so readily.

A warm solution of boracic acid in glycerin, mixed with a little alcohol, liberates the unchanged blue chlorophyll from the dried barium compound.

5. The blue chlorophyll exhibits two absorption bands in the red, close together; in the less refrangible region of rays one overlies B and the other overlies C. There is a feeble band near D.

6. Concentrated solutions of yellow chlorophyll in benzene are brownish in colour, and exhibit a magnificent red fluorescence.

When blue and yellow chlorophyll are separately treated with formic acid and ether, there are produced two new substances showing absorption-bands in the green. It is believed that when these bands have been observed, either in preparations of chlorophyll or in living tissues, that the chlorophyll has been altered by oxidation of formic aldehyd in the plant. The oxidation could be caused in living tissues by an excessive degree of illumination, which causes the destruction of the tissues, and otherwise by exposure of the contents of the plant cells to air or oxygen. An excessive illumination causes an exceedingly great activity in decomposing carbonic acid, and probably oxygen cannot be respired sufficiently rapidly; hence there may be a reverse action, or an oxidation of formic aldehyd to formic acid.

The leading characteristics of unaltered leaf-green are those of blue chlorophyll, namely, an intense absorption in the red, stronger even than in the violet or ultra-violet.

94. "Note on Dibenzanilide." By J. B. COHEN, Ph.D. In consequence of the appearance of the papers of Paal and others, and of Piçet (*Berichte*, 1890, 2587 and 3011), the author describes the results of experiments made some time ago. He comes to the conclusion that up to the present dibenzanilide has not been prepared; at any rate, not in the pure state. He finds that on heating benzanilide with acetic anhydride and a small quantity of fused sodium acetate, it is converted into acetanilide.

A meeting of the Research Fund Committee will be held in December. Fellows desiring grants are requested to forward their applications to the Secretaries before December 13th.

ROYAL INSTITUTION OF GREAT BRITAIN.
General Monthly Meeting, December 1, 1890.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D., F.R.S.,
Treasurer and Vice-President, in the Chair.

THE following gentlemen were elected Members of the Royal Institution:—Messrs. Charles Arthur Aikin, F.R.C.S., Louis Brennan, A. M. Dunlop, Henry Gourlay, John Rose Innes, B.Sc., B.A., Maurice Marcus, Charles Gibson Millar, and George Danford P. Thomas, M.D., M.R.C.S.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

Shortcomings of Denaturised Spirits for Burning.—C. Reinhardt (*Zeit. Angew. Chemie*).—Such spirit often attacks metals, e.g., brass lamps, fills the wicks with the salts of zinc and copper, and rapidly destroys platinum crucibles. According to Schenkel (in the same journal), this mischief is not due to the presence of pyridine bases and wood spirit, but to the fact that many dealers add an acid to the denaturised spirit to diminish its odour. This addition has subsequently been interdicted.

NOTICES OF BOOKS.

Fuels; Solid, Liquid, and Gaseous. Their Analysis and Valuation. For the Use of Chemists and Engineers. By H. J. PHILLIPS, F.C.S., Analytical and Consulting Chemist to the Great Eastern Railway Company. London: Crosby Lockwood and Co.

THIS little book will, we feel sure, be welcomed by the class of persons to whom it is more especially addressed. In our days it is felt necessary to select for every purpose that kind of fuel which is found to be the most suitable and in addition to obtain from each kind the maximum duty which it is capable of performing. For this purpose both a correct analysis and a determination of calorific value become frequently necessary, and to this end the author gives in brief the most suitable methods.

For the analysis of gaseous fuels he recommends the apparatus of Elliot, which is here described and figured. He has found it suitable for "quick working and reasonable accuracy." Certain more delicate procedures are inapplicable where time is a great object. For the estimation of the small quantity of nitrogen usually found in fuel the Dumas process is recommended. The calorific value of solid and liquid fuels is directed to be effected by means of Thompson's calorimeter.

There is a valuable selection of tables giving practical results and analyses. Thus we find the average composition of coal from various localities, that of various anthracites, the progressive diminution of hydrogen and oxygen from wood to anthracite, the analysis of patent fuels, the composition of water-gas, the gases occluded in coal, composition of oil-gases, &c. In fine, the work ought to have its place in the laboratory of every metallurgical establishment, coke manufactory, and wherever else fuel is used on the large scale.

Manchester Technical School. *Introductory Addresses on Technical Teaching in its Application to Trades and Industries Delivered at the Opening of the Session 1889-91; Together with the Address Delivered by SIR PHILIP MAGNUS, on the Occasion of the Annual Distribution of Prizes, Saturday, October 4, 1890.*

THIS pamphlet contains addresses on the "Engineering Trades," by Alderman W. H. Bailey; on the "Building Trades," by Frederick Smith; on the "Textile Trades," by J. R. Barlow; on the "Printing Trades," by Alderman H. H. Bemrose; on the "Chemical Trades," by Ivan Levinstein, and on the "Plumbing Trade" by J. Smeaton, as well as the Address by Sir P. Magnus.

There is in these addresses very much which of necessity withdraws itself from the purview of the CHEMICAL NEWS. Most of the arts discussed in these addresses are mechanical, not chemical. Not only so, but the economical and semi-political point of view here taken, and that quite justifiably, is not open to us.

There are, indeed, many golden utterances which we can only hope will sink deeply into the minds of the hearers and of the public. One of the speakers quotes from Adam Smith the saying: "The art of seeing governs the whole conduct of human life." Precisely so, and yet we have made education, from the Board School up to the University, to turn on words and abstractions. We have cultivated what a recent writer terms the "vice of inobservance." We are here rightly told that the "all round man is of little value." Yet we still try to develop all-round men.

Says another speaker, wisely enough, of the British workman, "if he will only do himself justice by mastering the theory as well as the practice of his trade, and by avoiding the pitfalls of drink and betting, the fact of his higher wages and shorter hours of labour will not place him behind his foreign rivals." There is here an admission that in technical education "we have still much leq-

way to make up" and that "we have been spending our energies upon discussions as to the rival claims of Board and Denominational schools." Might it not have been said that we have lavished our means in forcing elementary literary education upon those who do not want it, instead of putting higher, scientific, and technical training within the reach of those who need it? It is greatly to be deplored that the authors of the addresses do not seem to admit that one of the chief shortcomings of English education is its examinal character, with the accompaniments of "standards" and "payments by results." Another defect is that the management of education so largely devolves upon the nominees of political factions and religious sects.

Mr. Levinstein's very able and interesting address on the Chemical Trades announces one of the greatest misfortunes to India, and consequently to Britain, which have happened for a long time. A Swiss chemist, Professor Hemmann of the Zurich Polytechnicum, has at last invented a method of making artificial indigo at a reasonable price. A compound known as phenylglycocine, obtained by the action of monochloroacetic acid upon aniline, can be converted into indigo by merely heating with caustic alkali. Unless some great improvement can be effected in the cultivation of the indigo-plant there is great reason to fear that the indigo-districts of India may share the fate of the madder-districts of France.

Mr. Smeaton remarked that working in lead is little understood on the Continent, and that all the best work in Berlin, Dresden, Vienna, and other cities is done by Englishmen. He mentioned, however, that in London and other great cities plumbing work is falling more and more "into the hands of builders and contractors who do not understand plumbing, and care nothing about it so long as the contract is executed at a profit." Of this sort of work the speaker gave some startling instances.

These addresses, as they stand, are of exceeding value. Had the speakers recognised the folly of the examinal system, and especially of competition in education, they would have been simply priceless.

Manual of Assaying Gold, Silver, Copper, and Lead Ores. By W. LEE BROWN, B.Sc., of Chicago. Revised, Corrected, and Considerably Enlarged, with a Chapter on the Assaying of Fuels. By A. B. GRIFFITHS, Ph.D., F.R.S.E., F.C.S., &c. London: Heinemann.

WITH the exception of the chapter on fuels this work is a re-issue of a manual which has given great satisfaction in the United States.

Certain matter has been retained which is of questionable use in England. Thus, in the chapter on apparatus we are repeatedly referred to "Troemner's list." This price list is not to be found in England unless specially ordered.

"Casseroles" is apparently the American name for a porcelain evaporating-basin fitted with a handle. Generally speaking, the account given of apparatus, reagents, and manipulation corresponds with that which we find in the most approved manuals of analytical chemistry.

Mr. Brown, in drawing a line between assaying and analysis, depends on the method employed. The discovery of the composition of any substance by means of dry reagents and heat is an assay. The same determination mainly by the use of wet reagents, with or without the aid of heat, is an analysis. We are not sure that this distinction can always be followed. What, for instance, is the determination of the ultimate composition of an organic compound? The ores and metals for which special directions are given are gold, silver, copper, and lead. The author admits that none of the furnace methods for the determination of copper and lead give very accurate results. For copper he gives as much more accurate the volumetric process, and above all, the electrolytic method of Luckow.

But in the appendix we find a passage which must be pronounced "rule of thumb in excelsis." The writer, Mr. G. Nixon, says that "in a certain sense no one cares to know the ultimate amount of metal that an ore contains. What is desired in practice is the yield under the most skilful treatment, and this information is approximately obtained by fire for copper." Surely the rational industrialist will need to know how far his "most skilful treatment" falls short of the truth, and is still capable of amendment. Time was when the Cornish assay was the only method available. But what excuse can there be in these days for retaining it and analogous methods?

In the chapter on the examination of fuels, instructions are given both for its analysis and for its calorimetric examination.

For the examining of furnace gases the author describes and figures Bunte's apparatus as made by P. Harris and Co.

We regret to find that the author in speaking of "parting" makes use of Baumé's hydrometer scale instead of Twaddell's, or of direct specific gravity.

Our opinion of this work, as a whole, is distinctly favourable.

Anleitung zur Darstellung Chemischer Präparate, ein Leit faden für den Praktischen Unterricht in der anorganischen Chemie. "Introduction to the Preparation of Chemical Products; A Clue for Practical Instruction in Inorganic Chemistry." Von Dr. HUGO ERDMANN, Privat Dozent an der Universität Halle. Frankfurt am Main: Bechhold.

IT has long been found necessary to devote special treatises to the analytical department of chemistry, and it is now perceived that the synthetical department also requires a more thorough treatment than it can receive in the general text-books.

As far as inorganic chemistry is concerned, Dr. Erdmann makes a very successful effort to meet this want. He has had the advantage of working for five years as assistant to Prof. Volhard, to whom he declares himself indebted for various trustworthy methods which so far are not generally known. As far as possible he sets out from cheap or worthless materials, from by-products and residues which are apt to accumulate in the laboratory. The finished products, on the other hand, are largely such as are in constant use, and are at the same time not always to be met with in trade of sufficient degree of purity. Methods are given for the production of 10 per cent sodium amalgam, of sodium nitrite, of pure silver, both crystalline (according to Stas) and molecular, from residues, mercuric chloride, and platinum chloride, both from residues, hydrogen peroxide, &c. A curious printing fault in the preface puzzled us for the moment. It reads, "The beginning (Anfang) of the book discusses briefly some of the most essential laboratory appliances, &c." It should be "The appendix (Anhang)" &c.

We must pronounce this little work an excellent guide for instruction in inorganic chemistry.

Bechhold's Handlexicon der Naturwissenschaften und Medizin. ("Bechhold's Manual Dictionary of the Natural Sciences and Medicine.") Bearbeitet von A. VELDE, Dr. W. SCHAUF, Dr. V. LOEWENTHAL, und Dr. J. BECHHOLD. Frankfurt am Main: Bechhold.

WE have here the first part of what promises to be a very useful work. It is not an encyclopædia, but a dictionary explaining the technical language of the sciences. It is calculated to be useful not only to the cultivated laymen, but even to the *savant* in subjects outside his own speciality. The work is to be completed in ten parts of 64 pp. each. The descriptions are concise, but clear. Great use has been made of abbreviations, which are duly explained in the beginning of the work and present no difficulty. After the term to be explained follows first the

branch of science to which it belongs, and at the end of each such paragraph there is given the derivation of the word. We observe only two typographical errors: *acidum chronicum* instead of *chromicum*, and *Almus viridis* instead of *Alnus*. Some readers may possibly be puzzled by finding the names of certain chemicals given in the peculiar Latin guise used by German physicians and pharmacists. Thus "*ammonium chloratum*" stands not for ammonium *chlorate*, but for the corresponding chloride. Thus, even the suggested re-introduction of Latin as the universal language of science (though vastly preferable to Volapük) would not give us uniformity of nomenclature. This hand-lexicon will be very useful to all who have occasion to consult German scientific works.

Report of the Committee on Spelling and Pronunciation of Chemical Terms Appointed at the Toronto Meeting of the American Association for the Advancement of Science, August, 1889.

THIS pamphlet, for which we are indebted to the courtesy of Dr. Carrington Bolton, is a reprint from the *Proceedings of the American Association for the Advancement of Science*, vol. xxxviii. This Association, at a previous meeting, appointed a committee on the spelling and pronunciation of chemical terms. The committee sent out in May, 1889, a provisional list of words based upon the list drawn up by Prof. J. H. Appleton, and requested critical replies. A report based upon these replies was considered by the Chemical Section at the Toronto Meeting, when a further report was sent out to all American chemists. The "general principles" laid down are in many cases conflicting. Thus, it is recommended that "the pronunciation should be, as far as possible, in accord with the analogy of the English language, yet Continental pronunciation should be approached and present usage should be retained as far as possible. Many of the pronunciations laid down are in close accordance with those customary in Britain. We find, however, the *e* in methyl and ethyl marked short, which would probably involve ðther. In the four halogens the *i* in the last syllable is marked short. Words ending in *ide* or *id* are to be shorn of the final *e* and be pronounced chlorid, exid, &c. In words ending in *yl* the *y* is also to be short. Some of the suggestions seem very appropriate; thus the word "titre," or as written in America *titer*, is to be avoided. "Benzol" is justly considered undesirable. The authors do not approve of the proposal of Watts to make the names of basic compounds end in *ine* and those which are neutral in *in*.

We do not see how the words benzine and benzene, which do not signify the same substance, are to be distinguished. The termination *meter* occasions the committee some trouble. To distinguish micrometer (the instrument) and micrometer (the measure) they rely only on accents. In England we escape the difficulty by writing "metre" where it terminates the name of a measure. The pronunciation "tallic" laid down for "phthallic" will doubtless surprise many readers. The authors, we see, propose to use "radical" instead of "radicle," and to write "gram" for "gramme." This we consider a most objectionable innovation. Some scientific men, especially when writing for the press, have a habit of omitting the dot over the *i*, and thus it would often be impossible, in hurriedly written M.S., to distinguish between the words "gram" and "grain."

Upon the whole we should fear that the innovations in pronunciation proposed would render terms liable to be confounded with others.

The Committee does not appear to have taken any steps towards an international nomenclature in chemistry—a weightier matter than pronunciation. The English speaking nations still retain their needless terminations in phosphorus, chlorine, &c.; whilst the French cling to azote, and add the appendage *ine* to certain basic oxides, such as "lithine." We have repeatedly mentioned the

peculiarities of the Latin nomenclature used by German pharmacists, such as ammonium *chloratum* for ammonium chloride. But this subject can only be dealt with by a joint committee of English, French, and German chemists.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—Although Messrs. Lloyd and Teed deny that their circular had any resemblance to the official notices of the Chemical Society, there appears to have been a likeness sufficiently close to cause thirty-eight out of the "hundreds" who answered it to assume it to be an official notice, notwithstanding the request made by the writers to return answers to them.

The writers still decline to specify the real number of answers they have received, and how many were qualified in various ways; and I am, therefore, justified, since "hundreds" are named, in assuming that about 200, or say 12 per cent of the Fellows, agree with the proposals. This is scarcely enough backing for a somewhat ambitious programme.

Our self constituted guardians regret that anyone should have so poor an opinion of the "intellectual and moral status" of the Fellows as to suppose that they would assent to views put forth by the Council, and withhold assent from the same views advanced by private members.

For my own part I should regret extremely to see anything like a respectable number of the Fellows do the contrary. There is all the difference in the world between the two actions, and it by no means implies either intellectual or moral defect when assent is gladly given to a policy pursued by a lawfully elected and responsible body, and withheld from an identical policy proposed by a self-elected and irresponsible clique.

The words "Our present policy, which is to keep out of the society those who are intellectually or morally unworthy of the Fellowship," constitute, I think, an outrageous and insulting usurpation of the prerogatives of the Fellows and the Council.

Surely these gentlemen do not realise the immense responsibility they assume when, with such views publicly expressed, they or their friends proceed to blackball a candidate. What esoteric knowledge do Messrs. Lloyd and Teed possess by virtue of which they pronounce a candidate unfit "intellectually or morally" (after hearing his profession or calling read out) when five of their fellow members, presumably just as anxious for the welfare of the Society, have signed a declaration that he is a fit and proper person for election? What right have they to assume that Fellows are so careless, incompetent, or evil minded as to propose such candidates?

I think, sir, that if our two censors will quietly think matters over they will see that they have made a mistake, and will have the courage to withdraw from an untenable position,—I am, &c.,

R. J. FRISWELL.

115, Darent Road, N.
December 1, 1890.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—Will you kindly allow me to say that when signing the circular received some time since I was under the impression that it had in some way the support of the Council, and in doing so desired more to express a general

agreement with the idea that something ought to be done than a specific endorsement of each detail of the proposal?

I think with Messrs. Bloxam and Blount, that the best solution of the difficulty is for the Society to publish that it is not a qualifying body for professional chemists, and would suggest that a simultaneous publication of the existence and main function of the Institute should be made.

In this part of the world the F.C.S. reigns supreme, and the F.I.C. is practically unknown,—I am, &c.,

THOMAS FARRINGTON, M.A.

Analytical Laboratory,
4, Waterloo Place, Cork, Nov. 25, 1890.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Analytische Chemie.
Vol. xxix., No. 2.

The Presence of Arsenic in Commercial Zinc Oxide.—W. Stromeyer (*Archiv. de Pharmacie*).—The sample should be dissolved in hydrochloric acid and mixed with hydrogen sulphide water.

The Recognition of the Conclusion in Titrating Iron Chloride with Stannous Chloride.—F. H. Morgan.—From the *Journal of Analytical Chemistry*.

The Recognition of Mercury as Oxydimercuri-ammonium Iodide.—Joseph Klein (*Archiv. de Pharmacie*).—The author uses the action of ammonium chloride upon an alkaline solution of mercuric potassium iodide—a reaction which is the inverse of Messler's reaction for the detection of small quantities of ammonium salts. For detecting mercury in a dilute aqueous solution the author adds to a portion of it a little solution of potassium iodide and adds some soda-lye (lye of specific gravity 1.34 diluted with an equal volume of water), and a solution of ammonium chloride (10 parts of the solid chloride in 50 of water). If the solution is very dilute the test solution is superstratified.

Determination of Arsenic.—R. C. Canby (*Journal of Analytical Chemistry*).

Determination of Arsenic in Iron.—F. G. Müller, C. Reinhardt, and M. A. von Reis.—This memoir will be inserted as early as possible.

Removal of Arsenic Present in Determinations of Phosphorus.—E. D. Campbell.—From the *Journal of Analytical Chemistry*.

Detection of Nitrous Acid.—Curtman (*Phar. Central-Halle*) utilises the reaction of antipyrine with nitrous acid, depending on the formation of iso-nitrosoantipyrine. The reaction consists in the appearance of an emerald green colour.

Determination of Nitrous Acid in Presence of Nitric Acid.—Kalmann.—The nitrous acid is converted into nitric oxide gas by means of hydriodic acid according to the equation: $\text{NaNO}_2 + 4\text{HI} = \text{NaI} + \text{NO} + \text{I}_2 + \text{H}_2\text{O}$, and the nitric oxide formed is measured. The solution of hydriodic acid is prepared by dissolving at least twice as much iodine as is necessary for the decomposition of the nitrous acid in a saturated solution of potassium iodide, and lets solution of sodium sulphite flow in until the mixture is decolourised.

Determination of Nitric Acid.—F. H. Morgan and Edes Bates.—From the *Journal of Analytical Chemistry*.

Volumetric Method for Determining Carbon in Iron.—J. Wiborgh (*Berg der. Hütten Zeitung*).—This paper requires the accompanying illustration.

Determination of Graphite in Minerals.—J. B. Mackintosh.—From the *School of Mines Quarterly*.

A New Reaction for Thymol.—L. van Itallie (*Archiv der Pharmacie*).—If a few drops of potassa-lye are added to a liquid containing thymol and then iodised potassium iodide until the liquid has a faint yellow colour, a fine red colour appears on gently heating. The colour increases at first in intensity, but disappears soon afterwards. The reaction is said not to occur with other phenols.

Detection of Hydrosulphocyanic Acid.—G. Colasanti.—A dilute solution of this acid or of its salts gives a fine emerald green colour on the addition of a solution of copper sulphate (*Gazzetta Chimica Italiana*).

A Reagent for the Mercaptanes.—G. Denigès.—Already noticed under *Comptes Rendus*.

Action of Borax upon Polyatomic Alcohols and Phenols.—A. Lambert.—Noticed under *Comptes Rendus*.

An Improvement in Organic Combustions.—F. Blan (*Monats-Hefte für Chemie*).—The back end of the combustion tube, which is 114 c.m. in length, projecting 10 c.m. out of the furnace behind, and 19 in front, is closed with a caoutchouc plug through which passes a glass tube 10 c.m. long. In this a glass rod, 40 c.m. long, carrying at its front a strong platinum wire, can slide air-tight backwards and forwards. An air-tight closing is effected by means of a piece of caoutchouc tubing drawn tightly over the glass rod and the glass tube. By means of the rod the platinum boat, with the substance to be analysed, is moved backwards or forwards. To effect a firm connection between the wire and the boat there is a small appendage to the latter, having a narrow slit in its upright part. By thus rendering the boat movable, the combustion can be more nicely and easily regulated than heretofore.

Sources of Error in Determining Nitrogen by the Will and Varrentrap Process.—W. O. Atwater (*Amer. Chemical Journal*).

Determination of Iodoform.—M. Greshoff (*Chemiker Zeitung*).—A small quantity of the substance (0.1–0.5 grm.), is heated in a wide test-tube with 10 grms. of a 10 per cent solution of silver nitrate in the water bath. When cold any fatty matter is withdrawn by means of ether.

Quantitative Separation of Strychnine and Brucine.—J. E. Gerock (*Archiv. der Pharmacie*).—These bases, and especially their picrates, behave differently if heated with nitric acid. Brucine is coloured red by nitric acid, and on heating gives a yellow solution, which when carefully neutralised is not precipitated by picric acid. Strychnine does not suffer any chemical change from the action of nitric acid of 1.056 specific gravity (or weaker).

Determination of Nicotine by Polarisation.—M. Poporici.—The author's method requires the use of a table, for which we refer to the original.

The Quantitative Determination of Aniline and Monomethylaniline.—F. Reverdin and Ch. de la Harpe (*Chemiker Zeitung*).

A New Method for Determining Paranitro-Toluol.—F. Reverdin and Ch. de la Harpe (*Chemiker Zeitung*).—These two memoirs will be inserted as early as possible.

Researches on the Carbonic Acid in the Air.—W. Spring and L. Roland.—The particulars are not given.

Examination of Beer.—H. Schwarz (*Dingler's Polytechn. Journal*).—This paper does not admit of useful abstraction.

Determination of Acidity in Food-fats and Oils.—Gantler.—This is generally effected by dissolving the fat in ether free from acidity and titrating, using phenolphthalein as indicator. Gantler has checked the results with sensitive litmus paper, and has met with a rape-oil which turned the litmus paper very distinctly blue after

the addition of 2 c.c. alcoholic potassa, whilst the red colouration of phenol-phthalein did not appear until after the addition of 6 c.c. potassa solution.

Valuation of Indigo.—Ch. Tennant.—From the *Journal of the American Chemical Society*.

Eucalyptol.—Remarks on the sophistication of this oil.

Testing Glue.—R. Kissling (*Chemiker Zeitung*). This paper requires the accompanying figures.

Presence of Amber in Lakes.—W. Sonne (*Zeit. Angew. Chemie*).—The author's method turns on the recognition of succinic acid.

Chemical Examination of Blacking.—J. Hölbling (*Zeit. Ange. Chemie*).—The author tests for fatty matter, carbon, phosphoric and sulphuric acids, glycerin, iron, and extractive matters.

Determination of Benzaldehyde in Bitter Almond Water.—C. Denner (*Pharm. Central Halle*).—The author's process depends on the behaviour of benzaldehyde with phenyl-hydrazine.

Examination of Pharmaceutical Extracts.—A series of processes for which we must refer to the originals.

Detection of Diamines in Urine.—L. von Udränsky and E. Baumann.—An examination of a urine containing cadaverine and putrescine (pentamethylenediamine and tetramethylenediamine).

Determination of Urea.—Fowler mixes 1 vol. urine, the specific gravity of which is exactly known, with 7 vols. of solution of sodium hypochlorite, also of known specific gravity. The mixture is let stand for 2–3 hours and its density is re-determined. The difference of the values depends on the decomposition of urea, and on multiplication with 770 it gives the percentage of urea.

Occurrence and Detection of Indigo-red in Urine.—O. Rosenbach (*Berlin Klin. Wochenschrift*).—Urines which contain the chromogen of indigo-red yield with Jaffe's indican test no pure blue, but a more or less decided violet colour to chloroform.

Two Unusual Urine Pigments.—B. J. Stokvis.—A colouring matter found in the urine of a patient who had been taking resorcine resembled that of litmus. In another urine there was found a colour resembling, but distinct from, hæmatoporphyrine.

Detection of Albumen in Urine.—G. Roch (*Pharm. Central Halle*) finds that salicylsulphonic acid throws down albumen as a flocculent precipitate, even when present in so small a proportion as 0.005 per cent. The test is not affected by solutions of urea, uric acid, glucose, or peptone, or by normal urine.

Heller's Blood Test.—According to Filehne (*Virchow's Archiv*) this test may give a red, phosphatic deposit in the absence of the colouring matter of blood.

Determination of Alkalinity and Carbonic Acid in Blood.—A series of observations by different authorities for which we refer to the originals.

Detection of Carbon Monoxide in Hæmoglobine.—A. Welzel.—To 10 c.c. of undiluted blood are added 15 c.c. of a 20 per cent solution of potassium ferrocyanide, and 2 c.c. of an acetic acid made up by mixing 1 vol. of glacial acid and 2 vols. of water, and the whole is gently shaken. The coagulum in normal blood is black-brown, in blood containing carbon monoxide an intense light red. Or, the blood diluted with 4 parts of water is mixed with about three times its quantity of a 4 per cent solution of tannin. Blood containing carbon monoxide gives a bright crimson precipitate, which retains its colour for months. Normal blood gives a red precipitate at first, which in 1–2 hours takes a brownish shade, and in 24–48 hours turns to a permanent grey.

Detection of Tin in Confectionery.—J. Mayrhofer.—The author first destroys the articles in question with

nitric acid. To this end 20 grms. of the substance are covered with 50 grms. nitric acid (specific gravity 1.45), in a flask containing 400 c.c., and gently heated on the sand-bath until copious red fumes escape. When the main reaction is over, 10–15 c.c. of nitric acid are added at intervals of half-an-hour, heating gently, by which means the oxalic acid formed is mostly consumed. The decomposition lasts for half a day and requires 70–100 grms. nitric acid. The residue is placed in a porcelain capsule, the flask is rinsed out with 10 c.c. hydrochloric acid, and the whole evaporated to dryness. The residue is taken up in water and hydrochloric acid (about 100 c.c.), sulphuretted hydrogen is passed into the solution at 60–70° for half-an-hour, filtered when cold, the filter burnt, the ash reduced by ignition in a porcelain boat in a current of hydrogen, and the product of the reduction is dissolved in hydrochloric acid.

On Prout's Hypothesis with Reference to the Atomic Weights of Oxygen and Carbon.—J. A. Groshans (*Rec. des Travaux Chim. des Pays-Bas*).—On comparing the formulæ of different compounds which only contain hydrogen, oxygen, and carbon, the author concludes that the figures 12 and 16 must be admitted for carbon and hydrogen.

The Atomic Weight of Palladium.—E. H. Keiser, —(*Report of Chemical Section of Journal of Franklin Institute and Chemical News*).

Journal für Praktische Chemie.
New Series, Vol. xli., No. 11.

Researches from the Chemical Laboratory of Prof. A. Saytzeff at Kasan.—This contains a paper by A. Reformatzky on the Investigation of Linoleic Acid. The formula hitherto assumed for the composition of linoleic acid, $C_{18}H_{28}O_2$, is erroneous. Its true composition is $C_{18}H_{32}O_2$.

Researches from the Laboratory of the University of Freiburg.—These comprise a memoir by Ad. Claus and H. Burstert on the products of the chlorising of metaxylyl, and a paper by C. Willgerodt on a method of obtaining azohydrazines and polyazo-compounds.

A New Method for the Determination of Sulphur in Inorganic Sulphides.—P. Jannasch.—This memoir requires the accompanying figure.

In Reply.—F. Stohmann.—An answer to certain polemical comments by Herr Ossipoff on the combustion heat of fumaric and maleic acids.

Royal Institution.—The following are the Lecture Arrangements before Easter:—Professor Dewar, Six Christmas Lectures to Juveniles, on Frost and Fire; Professor Victor Horsley, Nine Lectures on the Structure and Functions of the Nervous System (Part I. The Spinal Cord, and Ganglia); Mr. Hall Caine, Three Lectures on the Little Manx Nation; Professor C. Hubert H. Parry, Three Lectures on the Position of Lullu, Purcell, and Scarlatti in the History of the Opera; Professor C. Meymott Tidy, Three Lectures on Modern Chemistry in Relation to Sanitation; Mr. W. Martin Conway, Three Lectures on Pre-Greek Schools of Art; The Right Hon. Lord Rayleigh, Six Lectures on The Forces of Cohesion. The Friday Evening Meetings will begin on January 23rd, when a Discourse will be given by The Right Hon. Lord Rayleigh on Some Applications of Photography; succeeding Discourses will probably be given by the Right Hon. Lord Justice Sir Edward Fry, Professor J. W. Judd, Professor A. Schuster, Dr. E. E. Klein, Mr. Percy Fitzgerald, Dr. J. A. Fleming, Dr. Felix Semon, Professor W. E. Ayrton, and other gentlemen.

Sizing Paper According to New Practical Experiments.—(From *Dingler's Journal*).—This paper will be noticed at some length as early as possible.

MISCELLANEOUS.

Diaries for 1891.—We have received from Messrs. Cassell and Co., publishers to Letts's Diaries Co., a selection of these well-known and old-established Diaries. The foolscap sizes, Nos. 31 and 48, interleaved with blotting-paper, are not only useful as Diaries, but they will be found convenient for the laboratory desk as rough note-books for jotting down results of experiments in progress, pending their record in the regular note-book. The smaller Diaries, Nos. 18, 23, and 26, give, besides the usual space for notes and memoranda, much new information on many subjects of daily enquiry. The Ladies Diary and Pocket Book gives, in addition, a table of Christian names and their meanings, useful in families where a name, male or female, has occasionally to be selected; it also gives, each month, for the benefit of young housekeepers, a list of articles of food in season. The Medical Diary keeps up its character, and contains much new information bearing on fees, doses, antidotes, nursing, &c. The Office Diary, No. 8, will perhaps be found the most popular, owing to its convenient shape and the fulness of the information at the beginning. It contains a Colonial and Foreign Banking, Postal, and Telegraph Directory, which is a marvel of compactness, and would be valuable to all who have much foreign correspondence if it were a little fuller in names of places which are now coming into notice.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Nickel Capsules.—(Reply to "C.")—Your correspondent will find some letters on the subject of nickel utensils in the *CHEMICAL NEWS*, about January, 1887.—T. F.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.**—Society of Arts, 8. (Cantor Lectures). "Gaseous Illuminants," by Prof. Vivian B. Lewes.
Medical, 8.30.
- TUESDAY, 9th.**—Royal Medical and Chirurgical, 8.30.
Institute of Civil Engineers, 8.
- WEDNESDAY, 10th.**—Society of Arts, 8. "Electric Lighting Progress in London," by F. Bailey.
Pharmaceutical, 8.
Geological, 8.
- THURSDAY, 11th.**—Royal, 4.30.
Mathematical, 8.
Institute of Electrical Engineers, 8.
- FRIDAY, 12th.**—Astronomical, 8.
Physical, 5. "Some Experiments with Selenium Cells," by Shelford Bidwell, F.R.S. "Note on Electrolysis," and "Alternating Current Condensers," by James Swinburne.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1620.

A RAPID METHOD FOR THE ESTIMATION OF UREA IN URINE.

By C. J. H. WARDEN,
Professor of Chemistry, Medical College, Calcutta.

As Mr. Sutton has remarked, the sodic-hypobromite method of estimating urea in urine has given rise to endless forms of apparatus, the principle of construction being in all cases similar. With the exception, I believe, of Lunge's nitrometer—when it is used for the estimation of urea—in all the instruments hitherto proposed the decomposition of the urea by the hypobromite has been accomplished in one apparatus, and the evolved gas measured in a separate tube. In the method now described, the evolved nitrogen is measured in the same tube used for the decomposition of the urea, and the procedure is consequently much simplified.

The apparatus employed for the decomposition of the urea and measurement of the liberated nitrogen consists of a slightly modified form of Crum's well-known nitrometer. Crum's tube, as usually constructed, has a total length of 210 m.m., an internal diameter of 15 m.m., and a capacity of about 25 c.c.; the cup at the top having a capacity of a little over 2.5 c.c. The modifications desirable in adapting the tube for the estimation of urea may be thus summarised:—

(a). Trebling the length of the tube, and thus making it 630 m.m. long; the capacity being increased to 75 c.c.; while the internal diameter is not altered.

(b). Grinding on to the lower open end of the tube a glass stopper, on which two narrow grooves have been filed.

(c). Increasing the capacity of the small cup at the top of the tube to 5 c.c., and having it accurately graduated to hold 2.5 c.c. when filled to a certain mark.

(d). Using somewhat thinner glass than that employed in the construction of Crum's tubes, as no mercury is used in the process.

The tube is graduated on the principle of Russell and West's apparatus. Russell and West's gas measuring tube was graduated to be used with 5 c.c. of urine. It was found that 5 c.c. of a 2 per cent solution of pure urea evolved 37.1 c.c. of nitrogen, and this volume was taken as the basis of graduation.

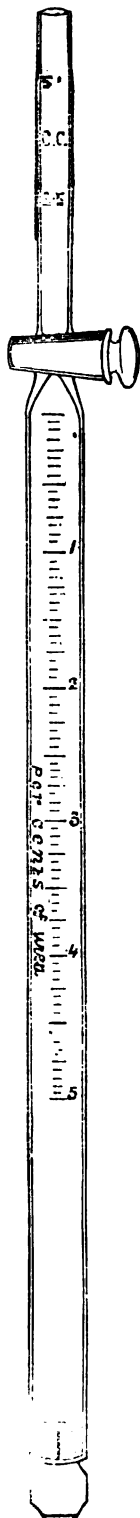
In the process now being described, only 2.5 c.c. of urine are used, and as 2.5 c.c. of a 2 per cent urea solution evolve 18.55 c.c. of nitrogen, this volume of gas will necessarily be equivalent to 2 per cent of urea; one per cent of urea is therefore equal to 9.27 c.c. of nitrogen, and the 9.27 c.c. volume is divided into ten equal parts, each part being equal to 0.1 per cent of urea; these divisions are further subdivided into two, each representing 0.05 per cent of urea.

The graduations should be continued so as to indicate up to 3 per cent of urea.

As in Russell and West's tube all calculations are avoided, the observed volume of gas at once indicating the percentage of urea in the specimen of urine under examination.

In using the apparatus the following solutions are required:—

1. A cold aqueous saturated solution of common salt-brine.
2. Hypobromite solution, made by dissolving 100 grms. of caustic soda in 750 c.c. of distilled water and adding 25 c.c. of bromine; this solution should be freshly prepared in small quantities as required for use.



To use the apparatus the stop-cock should be first slightly greased and closed, the tube inverted, and the grooved stopper removed.

The salt solution is poured into the tube to overflowing, the stop-cock opened to allow a drop or two to escape, and thus displace the small column of air in the bore of the stop-cock. The grooved stopper is then pressed home, the excess of brine escaping by the grooves in the side of the stopper, in the same manner as the superfluous fluid escapes through the capillary orifice in the stopper of a specific gravity bottle. In this way the tube is filled with the salt solution, all air being excluded.

The tube is now stood in a small trough of brine—a finger bowl answers very well—and supported by a filter-ring or clip, and the cup carefully dried.

The sample of urine to be examined is poured into the dry cup up to the 2.5 c.c. graduation, and any excess accidentally introduced removed by a fine fold of blotting-paper. The cup is then filled with water to the 2.5 c.c. mark, which is allowed to enter the tube, and this is repeated, the object being to free the cup from any traces of urine. The stopper is now removed, and the cup repeatedly filled with hypobromite solution, which is allowed to enter the tube until 40 c.c. of the solution or more have been used. When the addition of the hypobromite solution ceases to cause active effervescence, the tube is grasped by the right hand, the thumb being tightly pressed against the open end, and the contents thoroughly agitated.

The tube is again stood in the trough of brine, and when the temperature of the gas has reached that of the surrounding air, the volume is measured with the usual precautions; the volume of gas indicating the percentage of urea in the urine. Corrections for temperature and pressure can, of course, be applied if necessary.

In using the tube, if the evolved gas should exceed the volume yielded by 3 per cent of urea, the urine must first be diluted with an equal volume of water and 2.5 c.c. of the diluted urine used in the manner already described; the percentage of urea as indicated by the volume of gas being doubled. The froth which forms on the surface of the liquid in the tube can be dispersed by introducing a few drops of kerosene oil.

The points to which special attention may be drawn in connection with this method of estimating urea are—

1. Extreme simplicity of apparatus; all the various operations of measuring the urine, decomposing the urea, and measuring the volume of evolved gas, being performed with one instrument.

2. Ease and rapidity of manipulation.

3. Results as accurate as those afforded by any of the various modifications of Russell and West's original method.

Messrs. Cetti and Sons, of 36, Brook Street, Holborn, sole manufacturers, are prepared to supply these modified Crum tubes, and the well-known name of the

firm is a sufficient guarantee that the graduations will be accurate.

EXAMINATION OF OILS, FATS, AND ALLIED SUBSTANCES.

By THOMAS T. P. BRUCE WARREN.

IN examining oils, &c., no test should be considered as superfluous. There are some tests which are more important than others as regards their special significance, so that experience must decide the procedure to be followed in particular cases.

The specific gravity of an oil or mixture, if fluid, at 60° F., should always be noted at this temperature: fats, concrete oils, thick lubricating petroleum, should be taken at 100° F. The expansion of an oil is an important factor, the temperature at which it begins to show a divergence from the mathematical functions used in constructing a curve for constant or variable changes should also be noted. In this way we can frequently detect changes where chemical methods would be extremely troublesome even if possible.

A specific gravity bottle is constructed holding 25 c.c. to the neck, which is graduated and widened at the top into a funnel for the convenience of filling and retaining any oil beyond the capacity of the neck. The capacities of the bottle and the graduated neck are determined by pure mercury, so that the expansion due to the glass itself can be accurately measured and allowed for if required. It is preferable to distil the mercury direct into the bottle, otherwise the expulsion of air is very troublesome.

The difficulty of adapting different forms of Sprengel tube for this purpose led to the designing of this form of specific gravity tube. In using this it is immersed in water or oil to the upper mark of the neck. A platinum wire serves as a suspension for weighing or holding in an oil or water bath.

Knowing the capacity of the bottle, the specific gravity of an oil occupying the same bulk is easily determined.

The expansion of an oil is taken as being simply an arithmetical mean for the observed differences of temperature. This is certainly not correct; the first effect will be to expand A, the original bulk to $A + a$, a further increment of heat will expand A and a together, and so on for every successive increment of volume; consequently the expansion is in a geometrical ratio, and so long as no abnormal change takes place, we obtain a logarithmic curve in which the axes x and y follow a regular rate of variation. If on the axis x we represent the thermometrical increments, then y will show the corresponding volumes.

When something happens which makes the curve change with respect to its initial ordinates, it is a common thing to say that an interpolation formula must be introduced. Now whenever this occurs there must be some change to explain; either the capacity for heat has altered, so that an increased temperature no longer produces an uniformly corresponding mechanical effect, or some chemical change has crept in which upsets the previous mathematical relation of x and y .

We can discard for the present the examination of these points by polar co-ordinates and endeavour to find out by chemical methods what is really taking place. We know by the curve when a change has begun, and we can also tell between what points the change is uniformly constant; another interpolation or point in the curve indicates another change, and so on. At all these points an oil should be examined when cooled down to the original temperature. Some oils are more stable than others at the same temperature, and a mixture of two oils, such as olive and sesame oils, can be readily detected. The chemical change is due mainly to the loss of glycerin and to the partial oxidation of the fatty acids thus set free.

Oils which are easily oxidised are best heated in a flask with a bent neck dipping under mercury, or in connection with a vacuum pump.

The iodine absorption of an oil, if taken before and after heating, shows a diminished absorption which may be due to oxidation or other causes. Sulphur chloride shows that glycerin has been expelled.

In some cases it is useful to know the rate at which an oil absorbs oxygen, and how the same is expended; a measured volume of the gas contained in a graduated gas tube with an outlet at the top, standing over mercury is connected with a suitably constructed flask containing the oil, the air in which has been displaced by oxygen, the volume of which is noted. The residual gas in the tube is analysed; the CO_2 represents approximately the glycerin set free, and the deficiency of O beyond this shows what the oil and fatty acids have retained.

"The Oxidation of Lubricating Oils," by Dr. O. Bach, was given some time ago in the *Chemiker Zeitung*. This interesting paper will be referred to when dealing with machine oils.

THE VISCOSITY OF LUBRICATING OILS.

By H. JOSHUA PHILLIPS, F.C.S.

THE viscosity of an oil used for the lubrication of all kinds of machinery, cylinders, &c., being such an important factor in its specific selection, it becomes important that a recognised standard viscosimeter should be used by oil merchants and buyers, so that in drawing up a specification definite viscosities at definite temperatures (which would be decided according to what purpose the oil was proposed to be used), could thus be stated. It is well known that many cylinder mineral oils now in the market, although very viscous at the ordinary temperature, would be far too thin to be used at the working temperature of a cylinder.

Sacker's viscosimeter, an apparatus much in use for determining viscosities of oils, is practically useless to base any specification upon, since it is very rarely that any two of them will be found to give the same results with the same oil, owing to differences in bore and shape of constriction of the graduated tube and the length and bore of the protruding capillary tube; and moreover, the apparatus is not supposed to determine viscosities above the boiling-point of water. The apparatus which commands itself for uniformity and accuracy of results is that devised by Mr. Boverton Redwood, F.R.S.E., &c. (*vide Jour. Chem. Soc. Ind.*, v., 126). It is made of copper, the exit portion being agate, of definite bore and limited protuberance. Each apparatus is accurately standardised by Mr. Redwood himself, average rape-oil being taken as unity.

By using such an apparatus, there should be no difficulty with oil merchants and brokers in sending samples of oils of prescribed viscosity at stated temperatures, which would thus limit the shoals of specifically useless oils that one is often obliged to test and report upon.

G.B. Ry. Laboratory, Stratford, London, E.

ON THE SO-CALLED II., OR COMPOSITE HYDROGEN SPECTRUM OF DR. B. HASSELBERG.†

By Prof. A. GRÜNWALD.

BALMER has shown in the "Transactions of the Naturalists' Society" (*Wiedemann's Annalen*, xxvi., p. 80) that the wave-lengths of a part of the rays in the line-

* July 10th, 1889.

† Read before the Imperial Academy of Sciences, at Vienna, April 17th, 1890.

spectrum of hydrogen, $H\alpha$, $H\beta$, $H\gamma$, $H\delta$, have simple rhythmical relations to each other, so that any one of these wave-lengths may be represented by the formula—

$$\lambda = h \frac{m^2}{m^2 - 4}$$

($m=3, 4, 5, 6 \dots$) h being independent of m .

If we put $m=n+2$, we have then for the wave-lengths of the rays in question: $\lambda_1, \lambda_2, \lambda_3, \lambda_4 \dots$ the formula—

$$\frac{1}{\lambda_n} = \frac{1}{h} \left(1 - \frac{4}{(n+2)^2} \right),$$

($n=1$) ($1, 2, 3, 4 \dots$), and there exist the proportions—

$$\frac{1}{\lambda_1} : \frac{1}{\lambda_2} : \frac{1}{\lambda_3} : \frac{1}{\lambda_4} \dots : \frac{1}{\lambda_n} \dots = 1 - \frac{4}{3^2} : 1 - \frac{4}{4^2} : 1 - \frac{4}{5^2} : 1 - \frac{4}{6^2} \dots : 1 - \frac{4}{(n+2)^2}$$

The minute examination which the author undertook towards the end of last year on the II., or so-called compound hydrogen spectrum of Dr. B. Hasselberg, which he (Prof. Grünwald) is about to communicate to the Imperial Academy under the above title, led to the very remarkable result that a large part of it can be resolved into a finite number of groups of rays, whose corresponding wave-lengths, $\lambda_1, \lambda_2, \lambda_3 \dots \lambda_n$, have rhythmic relations to each other.

To each of the homologous wave-lengths of the different groups of this kind there corresponds a value of the independent factor h in the first formula.

From this discovery, the numerical demonstration of which admits of no doubt, the primary atoms of the hydrogen molecule in question, which emit the above mentioned series of groups of rays, consist of very numerous atomic particles forming a nucleus of maximum density, and form around this a series of separate strata or rings, the density of which decreases with the distances of the strata from the nucleus. If we give these strata from the outermost to the nucleus, the numbers $1, 2, 3, 4 \dots n$, these densities are as the rational numbers—

$$1 - \frac{4}{3^2} : 1 - \frac{4}{4^2} : 1 - \frac{4}{5^2} : 1 - \frac{4}{6^2} \dots : 1 - \frac{4}{(n+2)^2}$$

The atoms thus constituted are the primary atoms "a" of hydrogen $H = ba_4$.

If we assume, as it is most natural, that the agglomerations of the simplest chemical atoms consist of a great number of atomic particles (which, again, may be the simplest agglomerations of the ether) and take place according to the same laws as do the systems of stars according to the hypothesis of Kant and Laplace, *e.g.*, the group of stars in Andromeda, it follows at once that the primary atoms "a" of hydrogen must have approximately the stratified structure of the nebula in Andromeda, as shown photographically by Isaac Roberts, in December, 1888.

The primary element, "b," must have a much more complicated structure, on account of its higher valence.

ACTION OF THE GAS FROM As_2O_3 AND HNO_3 UPON *p*-OXYBENZOIC ACID.*

By EDGAR F. SMITH.

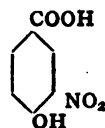
In vol. viii., p. 99, of the *American Chemical Journal*, I called attention to the fact that when methyl salicylate, in ethereal solution, was exposed to the gas arising from arsenic trioxide and nitric acid, ethers of α and β -meta-nitro-salicylic acids were produced. This procedure gave a ready method for the production, as well as an easy means of separating these two acids, the ether of the

α -acid being readily soluble, while that of the β -acid was practically insoluble in ether.

The ethyl ether of meta-oxybenzoic acid, in ether, gave when acted upon as above ethers of β -nitro-meta-oxybenzoic acid (m. p. $230^\circ C.$) and trinitro-meta-oxybenzoic acid (m. p. $171^\circ C.$). The details of this investigation may be found in the *Proceedings of the American Phil. Soc.*, September 7, 1888. I have recently experimented in the same line with *p*-oxybenzoic acid. The starting point was ethyl para-oxybenzoate, prepared according to the recommendation of Hartmann in the *Journal für Praktische Chemie* [II., xvi., 50. The ether thus obtained, after crystallisation from water, gave the constant melting point $112.5^\circ C.$, as stated by Graebe (*Annalen*, cxxix., 146), and not $116^\circ C.$, as given by Hartmann. The pure ether was next dissolved in ordinary ether, and the solution then acted upon for one and one-half hours, in the cold, by the vapours from nitric acid and arsenic trioxide. The flask containing the ethereal solution was corked and allowed to stand in a cool place for several days, after which the ether was distilled off. The residue was dark and oily, but after several hours became solid and crystalline. By solution in hot alcohol and re-crystallisation long, stout, red-coloured needles were obtained. These melted regularly at 69° – $70^\circ C.$ Barth (*Jour. f. Prakt. Chemie*, c., 369), speaking of the action of nitric acid upon ethyl *p*-oxybenzoate, mentions two products, ethyl nitro-para-oxybenzoate and ethyl dinitro-para-oxybenzoate. His description of the mononitro ether is so meagre that I was not able to determine at first whether I was dealing with a well-known compound or an entirely new product. The subsequent analysis of the free acid left no doubt as to the identity of my compound and that described by Barth. This chemist remarks that the melting-point of the nitro-ether lies below $-100^\circ C.$, I have found it as above -69° to $70^\circ C.$ On boiling the ether with caustic potash for some time and then acidulating the alkaline liquid a crystalline mass separates. It dissolves readily in hot water, crystallising from it, on cooling, in long needles with a faint yellow colour. At times the needles showed a flesh-red colour; this was removed by boiling the aqueous solution with animal charcoal. When pure the acid melted at 184° – $185^\circ C.$, the same as the acid obtained by Barth. A nitrogen determination, made by Mr. Seal of this laboratory gave 7.95 per cent N. The required N for a mononitro-*p*-oxybenzoic acid is 7.65 per cent.

An attempt to estimate the nitrogen in the ether by the Kjeldahl method failed.

Griess (*Berichte*, xx., 480) also obtained nitro-*p*-oxybenzoic acid of melting-point $185^\circ C.$, and showed that it was identical with the acid he had previously prepared from *p*-amidonitro-benzoic acid by boiling with KOH, so that its constitution and that of the acid prepared by me as above described is undoubtedly—



Hasse (*Berichte*, x., 2188) states that nitro-*p*-oxybenzoic acid contains water of crystallisation. The acids of Barth, Griess, and myself are anhydrous.

While *p*-nitro-oxybenzoic acid requires a large volume of hot water for its solution, its sodium salt is very soluble, and from its concentrated liquid separates in beautiful red coloured needles forming bundles.

The amide of the acid ($C_6H_3(NO_2)OH.CONH_2$) consists of beautiful orange-yellow coloured tufts. It melts at 160° – 161° , and dissolves easily in hot alcohol.

The above account concludes my study of the action of the vapours from nitric acid and arsenic trioxide upon the three hydroxy-benzoic acids. The results briefly summarised are these:—

* From the Chemical Section of the *Journal of the Franklin Institute*, December, 1889.

With ortho-oxy-benzoic acid two nitro acids were obtained; with meta-oxy-benzoic acid one nitro acid and a tri-nitro-meta product resulted; and with para-oxy-benzoic acid, one meta-nitro acid.

The course of the reaction in these three cases (the *m*-oxy-acid excepted) was not attended by any troublesome intermediate products, and for this reason the method may perhaps become serviceable in the nitration of other oxy-acids.

THE ACTION OF HYDROGEN SULPHIDE GAS UPON METALLIC AMINES.

By EDGAR F. SMITH and HARRY F. KELLER.

WHEN pure, dry hydrogen sulphide gas was conducted over palladammonium chloride, $\text{Pd}(\text{NH}_3\text{Cl})_2$, no change occurred in the appearance of the compound. However, on applying a gentle heat (70° – 80° C.) to the boat containing the metallic amine, the latter gradually assumed a black colour. This change extended throughout the entire mass. Upon increasing the heat ammonium chloride was volatilised. The residue was found to consist of palladium and sulphur. Single mineral acids were without effect upon it. Aqua regia attacked it very slowly.

I. 0.3790 grm. of $\text{Pd}(\text{NH}_3\text{Cl})_2$ gave 0.2498 grm. of the black sulphide. Assuming that the latter is represented by the formula PdS , the required monosulphide for the quantity of palladammonium chloride used would be 0.2484 grm.

II. 0.2795 grm. $\text{Pd}(\text{NH}_3\text{Cl})_2$ gave 0.1822 grm. sulphide, while the calculated amount should be 0.1831 grm.

This behaviour of the palladammonium chloride led us to expose the following metallic amines to the action of hydrogen sulphide gas:—

Purpureo-Cobaltic Chloride ($\text{Co}_2\text{Cl}_6, 10\text{NH}_3$).—0.5287 grm. of this substance, finely divided, were weighed out in a porcelain boat. The latter was placed in a combustion tube of hard glass. This was in connection, on the one side with a drying apparatus, on the other with a Peligot tube containing water. The latter served to produce a back-pressure of the gas, and in this manner the boat and its contents were constantly surrounded by an atmosphere of hydrogen sulphide. The gas was at first allowed to act in the cold. It produced an immediate change. The cobalt amine assumed an intense black colour. To all appearances the change was complete in a few minutes, and extended through the entire salt. On the application of a gentle heat (80°) ammonium chloride volatilised. Later the heat was raised, and a current of carbon dioxide substituted for the hydrogen sulphide. The boat was allowed to cool down in the gas. The final product was dense, and black in colour. Its weight was 0.2258 grm. Assuming the change of the amine was to sesquisulphide the amount of the latter, corresponding to 0.5287 grm. of the amine, would weigh 0.2253 grm. On examining the sulphide it was found to consist of sulphur and cobalt.

Roseo-Cobaltic Sulphate ($\text{Co}_2(\text{SO}_4)_3, 10\text{NH}_3 + 5\text{H}_2\text{O}$).—This salt, too, sustained an immediate change when acted upon in the cold by hydrogen sulphide. There was in addition a simultaneous evolution of moisture, and stellular, colourless crystals appeared on the walls of the combustion tube. These gradually dissolved in the water present, and imparted to it an intense yellow colour. The crystals were $(\text{NH}_4)_2\text{S}_2$. On gently heating roseo-cobaltic sulphate in a stream of hydrogen sulphide, it invariably happened that when a temperature of 70° C. was attained, the black mass, in the boat, swelled up considerably, and was projected into the tube. Some deep-seated change

occurred, which we are not prepared to explain at present.

Luteo-Cobaltic Chloride ($\text{Co}_2\text{Cl}_6, 12\text{NH}_3$).—This salt was affected by hydrogen sulphide in the cold, although heat was required to bring about a complete change. One quantitative determination gave the same result as was obtained with purpureo-cobaltic chloride, *i.e.*, that the product was evidently cobalt sesquisulphide.

Of the cobalt amines examined, the roseo-derivative was most rapidly changed by the gas. We have good reasons for believing that we can make this reaction serviceable in the determination of cobalt in these bases.

Purpureo-Chromic Chloride ($\text{Cr}_2\text{Cl}_6, 10\text{NH}_3$).—We exposed this salt for a long period, in the cold, to the influence of hydrogen sulphide, without its sustaining any alteration. On raising the temperature so that it was slightly lower than the dissociation temperature of hydrogen sulphide, the purple-coloured amine became quite black in colour. It had a velvety appearance and resembled the chromium sesquisulphide obtained by other methods.

I. 0.6390 grm. substance gave 0.2640 grm. sulphide. The theoretical amount should be 0.2629 grm.

When this sulphide is exposed to a high heat in a current of hydrogen gas, it parts very slowly with its sulphur.

It is our intention to apply this reaction to other metallic amines as soon as we can do so, though at present our work has been interrupted by unforeseen circumstances.

ON THE REMOVAL OF GOLD FROM SUSPENSION AND SOLUTION BY FUNGOID GROWTHS.*

By A. LIVERSIDGE, M.A., F.R.S., Professor of Chemistry
in the University of Sydney.

(Concluded from p. 279.)

Date.	No. 16.
11 10 89.	<i>Reduced by Ferrous Sulphate Solution.</i>
14 10 89.	Clear solution. Flocculent dirty bluish-green precipitate of gold.
1 1 90.	Pale green solution. Dirty green precipitate. No growth.
22 5 90.	Pale yellowish-green solution. Dirty green precipitate. No growth.
28 5 90.	Bottle coated with very thin film of gold. Bluish-black precipitate in powdery form, not coherent nor adherent to bottle. No growth. Solution colourless.
	No. 17.
11 10 89.	<i>Bread Crumbs.</i>
14 10 89.	Bread stained purple outside. Blue-purple solution. Neither growth nor precipitate.
1 1 90.	Pale blue solution. Bread stained blue-black. Slight fungoid growth on bread of a pale purple-blue colour.
22 5 90.	No further change.
28 5 90.	No further change.
	No. 18.
11 10 89.	<i>Potassium Tartrate Mould.</i>
14 10 89.	Purple-red solution. No precipitate. Mould stained purple.
1 1 90.	Thick, dark bluish growth. Pale blue solution.
22 5 90.	Thick, dark bluish growth. Purple slate-coloured solution.

* Read at the Chemical Section of the Franklin Institute, October 21, 1890.

* From the *Transactions of the Australasian Association for the Advancement of Science*, Melbourne Meeting, 1890, Section B.

28 5 90.—Solution colourless. Mould very voluminous, readily floating about, of a deep bluish colour. Growth $\frac{3}{4}$ of an inch across. Also a blue-black deposit.

No. 19.

Magnesium Sulphate Mould.

14 10 89.—Colourless solution. All gold precipitated. Mould stained dirty green.

1 1 90.—Slight dirty green precipitate. Mould dark green, but had not increased.

22 5 90.—No apparent alteration.

28 5 90.—Colourless solution. Slight blue-black precipitate. Mould blue-black also.

No. 20.

11 10 89. *Green Cheese Mould.*

14 10 89.—Purple-red solution. Cheese mould stained purple. No growth nor precipitate.

1 1 90.—Purple-blue solution and growth.

22 5 90.—Purple-blue solution and growth.

28 5 90.—Dark purple-blue solution. Blue-black growth on pieces of the cheese mould.

No. 21.

11 10 89. *Phosphorus in Turpentine.*

14 10 89.—Red-purple solution. No precipitate. No growth. Turpentine floating on top.

1 1 90.—Red (ruby) solution. Some whitish growth.

22 5 90.—Ruby solution. Some dark ruby-coloured mould in addition to the whitish growth.

28 5 90.—Solution red. Growth dark-red, mixed with some white.

No. 22.

11 10 89. *Phosphorus in Carbon Disulphide.*

14 10 89.—Pale purple solution, the carbon disulphide of a dirty colour.

1 1 90. Slate-purple solution. Adherent film of light slate-coloured deposit. No growth.

22 5 90.—No apparent alteration.

28 5 90.—Dark (slate) purple solution. No growth and no precipitate at bottom.

No. 23.

Oxalic Acid Mould.

11 10 89.—Deep purple in ninety minutes.

14 10 89.—Red purple solution. No precipitate, and mould had disappeared.

1 1 90.—Purple colour. No mould and no precipitate.

22 5 90.—Slight growth at bottom.

28 5 90.—Red-purple colour. No growth and no precipitate.

No. 24.

11 10 89. *Phosphorus in Chloroform.*

14 10 89.—Almost colourless solution. Chloroform at bottom of a pale purple-blue colour. No precipitate. No growth.

1 1 90.—Red-purple solution. No growth. A little black deposit.

22 5 90.—Pink-purple solution. A whitish growth. A little black precipitate.

28 5 90.—Pale ruby-red colour. Turbid (metallic) looking. Small quantity of purple-red growth in small heavy pieces. Also small pieces of a waxy-looking material, probably separated phosphorus.

No. 25.

Banana Skin Scrapings (Mouldy).

11 10 89.—Pale-purple in ninety minutes.

14 10 89.—Dark-purple solution. Skin stained. Slight precipitate.

1 1 90.—Dark purple-red solution. Growth on skin almost black.

22 5 90.—Dark blue purple solution. Growth on skin black. Dark growth at bottom of solution.

28 5 90.—Dark blue purple solution. Growth on skin purple-black. Also purple-black loose precipitate.

The details of the experiments are given since they show the first appearance of the mould and the time, taken for the change in colour according to the removal of the gold.

It is noticeable that no growth was produced where chloroform, turpentine, or carbon disulphide was used as the solvent for phosphorus, but alcohol favoured such growth. The development of the mould may be in part due to the presence of the alcohol radical (C_2H_5) ethyl existing in both ether and alcohol; the presence of phosphoric acid, we know, is as essential to penicillium as it is to man.

It is remarkable that the oxalic acid mould did not increase but disappeared (confirmatory experiments are required on this and other points). The organic substances, like bread, &c., behaved as might have been expected.

It was found by Roulin that the salts of iron and zinc promoted the growth of moulds; and Hamlet ("Australasian Association for the Advancement of Science," Sydney, 1888, p. 326), found zinc in the mould of mouldy bread, and it may be that many other metallic substances, including gold, are favourable to the growth of moulds.

There is no doubt that gold in natural waters could be removed by any moulds with which it might come in contact; but then any other organic matter, living or dead, does the same. Hence at this stage of the experiments I do not wish to draw any inferences as to the possible part which fungoid growths may have had in the separation and accumulation of gold in natural deposits, alluvial or otherwise.

THE DRY ASSAY OF TIN ORES.* PART II.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.
(Continued from p. 277).

V. Influence of Associated Minerals on the Assay.

THE minerals that are liable to remain with the black tin after the ore has been washed, roasted, and treated with nitro-hydrochloric acid, are quartz, felspar, mica, tourmaline, garnet, and columbite (tantalite). To test their influence, the minerals were ground fine enough to pass through a 60-mesh sieve, and any particles of iron coming from the implements used in grinding were removed by the magnet. The minerals were mixed with the black tin in the different proportions shown in the subjoined tables, and the effects studied which they have on the two best methods of assay,—the German method and the method of fusing with potassium cyanide. The charges were so regulated that the flux in the German assay was always equal to three times the quantity of the ore plus the mineral, and in the cyanide assay to six times the quantity. Four parts of cyanide were mixed with the ore; one part served as bottom for the crucible and one part as cover. In the German assay, the amount of borax glass was increased in proportion to the percentage of mineral added and that of salt decreased. The fusions were made in the usual way; the time for the cyanide assay had to be increased to not less than fifteen minutes before a tranquil fusion was obtained.

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 3.

TABLE XXII.

No. of assay.	Charge.							Resulting tin.	
	Ore. Grms.	Quartz.		Char-coal. Grm.	Bl. flux substitute. Grms.	Borax glass. Grms.	Potass. cyanide. Grms.	Grms.	Per cent.
		Grms.	Per cent.						
111.	5	1	16.66	1	18	1	—	3.280	65.60
112.	5	2	28.57	1	21	1	—	3.100	62.00
113.	5	3	37.50	1	24	—	—	3.035	60.70
114.	5	4	44.44	1	27	—	—	2.945	58.90
115.	5	5	50.00	1	30	—	—	2.565	51.30
					Bl. flux.				
116.	10	2.5	20.00	—	50	—	—	5.2	52.00
117.	10	6.6	40.00	—	66.4	—	—	4.3	43.00
118.	10	10.0	50.00	—	80	—	—	2.8	28.00
119.	10	15.0	60.00	—	100	—	—	1.0	10.00
120.	10	30.0	75.00	—	160	—	—	0.0	0.00
121.	5	1	16.66	—	—	—	24	3.285	65.70
122.	5	2	28.57	—	—	—	28	3.215	64.30
123.	5	3	37.50	—	—	—	32	3.195	63.90

TABLE XXIII.

No. of assay.	Charge.							Resulting tin.		Resulting alloy.	
	Ore. Grms.	Albite.		Char-coal. Grm.	Bl. flux substitute. Grms.	Borax glass. Grms.	Potass. cyanide. Grms.	Grms.	Per cent.	Grms.	Per cent.
		Grms.	Per cent.								
124.	5	1	16.66	1	18	1	—	—	—	3.475	69.50
125.	5	2	28.57	1	21	1	—	—	—	3.265	65.20
126.	5	3	37.50	1	24	1.25	—	—	—	3.010	60.20
127.	5	4	44.44	1	27	1.50	—	—	—	2.680	53.60
128.	5	5	50.00	1	30	2	—	—	—	3.615	52.30
129.	5	1	16.66	—	—	—	24	3.285	65.70	—	—
130.	5	2	28.57	—	—	—	28	3.275	65.50	—	—
131.	5	3	37.50	—	—	—	32	3.265	65.30	—	—

(1). The quartz used was the ordinary compact colourless variety.

The amount of soft slag found on top of the borax slag decreased in proportion to the percentage of quartz added, showing that a part of it had entered into combination with the borax slag. In assay No. 111 it was $\frac{1}{2}$ inch thick, in No. 115 only $\frac{1}{4}$ inch. Its structure was not so coarsely crystalline as usual. It grew finer, and the brittle slag became harder with increase of silica; the lustre remained the same; the colour varied from grey to bluish black. The borax slags increased in quantity as quartz was added, their vitreous character being somewhat impaired by the silica, and also their brittleness; the lustre remained uniform; the usual olive-green colour changed somewhat and became brownish. The buttons separated well from their slags, had the usual appearance, and were free from iron. The results obtained in Nos. 111 to 115 (see Table XXII.) showed a gradual decrease in the amount of tin recovered. This is, however, less than has been generally supposed from the figures of Berthier, Nos. 116 to 120, which are usually quoted.* Berthier,† as the writer understands it, mixes his siliceous ore with four times the amount of black flux. With the German method of charging the black tin with 67.84 per cent of tin mixed with 50 per cent of silica gave 51.30 per cent of metallic tin; Berthier's black tin containing 70 per cent of tin, with the same addition of silica, but mixed with the flux, gave only 28 per cent of tin, or 24.8 per cent less than is charged as in the German method. This shows the disadvantage of mixing ore with basic flux.

In the cyanide assays, Nos. 121 to 123, the slags showed uniformly a very coarsely crystalline structure and had a strong lustre. They were as opaque as usual, and became harder with the increase of silica. In No. 121 only the upper rim was parrot-green. This spreads in No. 122 so as to cover the entire surface; it is $\frac{1}{4}$ inch thick at the

circumference and $\frac{1}{4}$ inch in the centre; in No. 123, the thickness is uniformly $\frac{1}{4}$ inch. The appearance of the buttons is the same as if no silica had been added. The results show a decrease in the amount of tin recovered, but the loss is not so great as with the German assay.

(2). The felspar used was the compact albite that occurs so generally in the tin lodes; it has a very perfect cleavage, shows a pearly to a silky lustre, and is white with a tinge of grey.

Salt and borax slags of the German method, Nos. 124 to 128 (see Table XXIII.), are similar to those obtained when quartz was added to the ore. The buttons, however, are surrounded by a slag that is more stony than the borax slag above, and almost black. It adheres strongly to the buttons, and is liable to retain particles of metal. All the buttons were dark and dull; they were brittle, hard to cut, and contained iron, its presence being caused by the infusible character of the albite; the reduction was prolonged, and the ferric oxide of the cassiterite reduced before fusion took place, and alloyed with the metallic tin resulting from the more readily reducible stannic oxide. By examining the results, Nos. 124 to 128, it will be seen that, although all the buttons are ferruginous, the weight of the last four buttons is too low, showing that tin had also entered the slag, not enough iron being present to precipitate all the tin. The slagging is assisted by the intimate contact of the refractory felspar and the cassiterite. Owing to the character of the charge, stannic oxide, or even metallic tin, is liable to be slagged by the alkali carbonate, and stannous oxide by the silica.

The influence on potassium cyanide is seen by Nos. 129 to 131 (Table XXIII.). The upper white slag of pure cyanide with cyanate adheres to a lower porous slag of greenish grey colour, which encloses the buttons. These are white, bright, malleable, easily cut, and free from iron. The amount of tin lost, even if 37.50 per cent of albite is added to the ore, is only a little over 2 per cent. It is strange there should be so little difference between

* Mitchell, *op. cit.*, p. 483; Ricketts, *op. cit.*, p. 87.
† "Traité des Essais," 1847, vol. ii., p. 485.

the three assays which contain such varying amounts of albite. The only explanation seems to be that, at the low temperature at which the assay is carried out, the felspar is not decomposed, but remains suspended in the lower slag, which receives its greenish tinge from the iron of the cassiterite, and its grey from the felspar mixed with it. If the lower slag is boiled in water, it falls to pieces, leaving a residue that looks very much like the original pulverised albite after it has been moistened, except that it has a slight tinge of green, resulting from the iron.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

November 28, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

THE following communications were made:—

“Additional Note on Secondary Batteries.” By Dr. J. H. GLADSTONE, F.R.S., and W. HIBBERT, F.I.C.

After referring to the debateable points as to what compounds are formed and decomposed in the working of such batteries, the authors give the results of their examination of the red substance formed by the action of dilute sulphuric acid or minium, and which Dr. Frankland believes to be a compound having the formula $Pb_3S_2O_{10}$. The ultimate analysis showed 72 per cent of lead. A portion of the substance was treated with a 3 per cent solution of ammonium acetate, to dissolve out any normal sulphate that might be present; this left a residue much darker in colour than the original substance, and containing 82 per cent of lead. PbO_2 contains 86.6 per cent of lead. The colourless solution yielded a ratio of Pb to SO_4 varying from 2.0 to 2.15; pure $PbSO_4$ requires a ratio of 2.16, and Dr. Frankland's compound 3.23. From these results the authors conclude that the portion dissolved was not a basic sulphate, and that the evidence tells against the original substance being a chemical compound.

The authors have also continued their comparative experiments on the action of spongy lead on dilute sulphuric acid, either pure or containing a small quantity of sulphate of soda. After the experiments had gone on for five months, the residues were analysed. That from the pure acid showed 82 per cent of lead sulphate and 18 per cent of metallic lead; whilst that mixed with sodium sulphate gave 89 per cent of lead sulphate and 11 per cent of lead. They therefore conclude that although the action of acid on lead is initially diminished by the presence of sodium sulphate, the final result is rather the other way.

Mr. G. H. ROBERTSON, who had used ammonium acetate to analyse plugs from storage cells, said he had arrived at results much the same as those stated by the authors.

Mr. SWINBURNE said Dr. Frankland was absent, but without agreeing with him, he would suggest that Dr. Frankland might say that ammonium acetate decomposed the sub-salt $Pb_3S_2O_{10}$, and then dissolved the sulphate $PbSO_4$. The question might be attacked by acting on equal quantities of the substance and the mixture $PbO_2, 2PbSO_4$, in a calorimeter with ammonium acetate, to see if the same heat is produced; this would show whether the substance is a mixture or a compound.

Dr. S. P. THOMPSON was glad that the authors allowed a possibility of basic sulphate being formed, for it was well known that an almost irreducible sulphate resulted from leaving a cell nearly discharged; this, he thought, would point to a possible formation of a basic sulphate from PbO and $PbSO_4$. Mr. Swinburne did not see where the PbO came from, except in newly pasted negatives

he knew of no evidence of an intermediate stage of oxide on the plates. They appear to change directly to sulphate.

Dr. THOMPSON said that a rapid discharge was known to produce basic salts.

This Mr. SWINBURNE thought due to deficiency of acid near the plates. Peroxide, he said, could not be formed on the negative without the acid was heterogeneous and gave rise to local currents.

Mr. W. HIBBERT, referring to Mr. Swinburne's statement, said he had put one plate of spongy lead into strong acid, and another into weak, and from this arrangement obtained a fairly large current. As regards the basic sulphate spoken of by Dr. Thompson, he did not think there was much probability of its being formed. Time, he said, had an important influence on a discharged cell, and he would not expect to easily reduce the $PbSO_4$ formed by the long-continued action of lead on sulphuric acid.

The PRESIDENT enquired whether Mr. Hibbert's argument would apply to a fully charged cell.

Mr. HIBBERT in reply, said that in this case the time required to produce sufficient sulphate to be irreducible would be very much longer, for in a partially discharged cell much sulphate was already formed.

Dr. GLADSTONE said he had anticipated that Dr. Frankland would raise the objection referred to by Mr. Swinburne. As far as he was aware, there was no direct evidence either way, but he thought that the suggested decomposition was improbable. If he acted on a mixture of PbO_2 and $PbSO_4$, he would expect to get the results actually obtained. Mixtures, however, were difficult to deal with and the results not conclusive, for the physical condition of the mixture was not the same as that of the actual products. Referring to Dr. Thompson's remarks, he understood that it was the basic sulphate which he (Dr. Thompson) considered irreducible. Dr. Frankland, however, believed this sulphate more easily reduced than $PbSO_4$.

The PRESIDENT remarked that he thought Dr. Frankland had two reasons for his belief in the existence of the basic sulphates. One of these was the difficulty in reducing normal sulphate, whilst the other was based on the rapid fall of E.M.F. at a certain part of the discharge. It was at this point that Dr. Frankland thought the new sulphate formed, and to meet this argument it was necessary to find some other explanation of the rapid fall. In this connection he (the President) enquired whether there was sufficient peroxide formed on the negative plate to account for the drop.

On this point Dr. Gladstone could not speak decisively.

“An Illustration of Ewing's Theory of Magnetism.” By Prof. S. P. THOMPSON, D.Sc.

A number of small “charm” compasses were placed together on a glass plate of an ordinary vertical-attachment to a lantern. A large magnet at a distance served to neutralise the earth's field, and a coil enabled a magnetising force to be applied in the plane of the needles. By this apparatus all the various phenomena exhibited by Ewing's model were beautifully shown on a screen. In the course of his experiments Dr. Thompson had found that when small magnets placed at moderate distances apart were used, it was much more necessary to neutralise the earth's field, in order that they might set themselves according to their mutual attractions, than when larger magnets were employed. A weak field directed the small openly spaced magnets, whereas with larger ones their mutual actions were much more powerful. This fact, he thought, throw some light on the molecular grouping in magnetite (loadstone). This substance exists in two forms, viz., one crystalline and the other of a heterogeneous structure. The former variety exhibits no magnetic retentiveness, whilst the latter is decidedly magnetic. As far as he was aware no sufficient explanation had been given of the non-retentiveness of the crystalline variety. A difference in the molecular distances or groupings might account for the peculiarity.

Mr. BOYS said it was rather curious that Prof. Rücker had just devised a somewhat similar illustration of Ewing's theory, and he exhibited it at the meeting. It consists of little magnets made of long U-shaped pieces of watch-spring pivoted by glass caps on needle points; the needle points are fixed in little discs of lead stuck on a sheet of glass which forms the base of a glass box. An open helix surrounding the box serves to apply magnetic force.

Mr. SWINBURNE called attention to two theoretical points. First as regards susceptibility (which he regarded as a mere ratio and not a property), he said that if particles of iron at a high temperature rotate, as has been supposed, the susceptibility should be negative, and Prof. Ewing, he believed, had some reason to think that this was the case. The next point concerned the loss of energy when an armature rotates in a strong magnetic field; this, he said, was known to be considerable, whereas if Ewing's theory is correct he would expect little or no loss, for all the little magnets would always put themselves in the direction of the field and would never pass through positions of unstable equilibrium.

The PRESIDENT said he had discussed the question of negative susceptibility some years ago with Dr. Lodge with reference to the drop in the characteristics of dynamos, but he was not aware that any direct evidence had been obtained.

Prof. PERRY thought negative susceptibility might be possible in strong fields, but not in weak ones.

Mr. SWINBURNE, on the contrary, considered its existence would be more marked in weak fields.

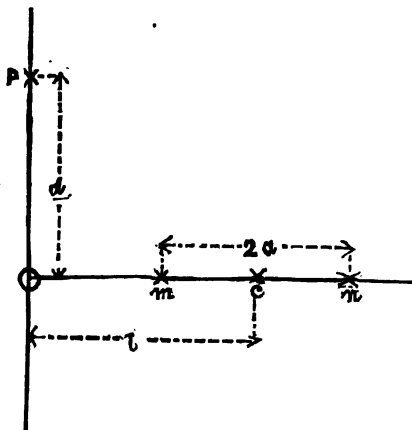
Mr. H. TOMLINSON said he had tried experimentally whether the susceptibility of nickel, when heated above its critical temperature, was negative, but he had not been able to detect it, although his apparatus was very sensitive.

"The Solution of a Geometrical Problem in Magnetism."
By THOMAS H. BLAKESLEY, M.A.

The problem referred to was the following:—Given the two poles of a magnet and a straight line intersecting at right angles, its axis produced, to determine at what point this line is parallel to the field. The question is of scientific interest, because if the point be found experimentally, the distance between the virtual poles of the magnet can be determined, whilst it is important practically from its bearing on the deviation of ships' compasses in certain cases.

The instances in which it would apply are pointed out in the paper.

Assuming the points m and n (see figure) to be the



positions of the virtual poles, and P the required point it is shown that—

$$\frac{m}{(d^2 + m^2)^{\frac{3}{2}}} = \frac{n}{(d^2 + n^2)^{\frac{3}{2}}}$$

where $om = m$, $on = n$, and $oP = d$. From this the expression—

$$\left(\frac{d^2}{2mn}\right)^3 - \frac{d^2}{2mn} - \frac{1}{2} \frac{m^2 + n^2}{2mn} = 0$$

is deduced.

Now in hyperbolic trigonometry we have a formula—

$$\cosh^2 \theta - \frac{1}{2} \cosh \theta - \frac{1}{2} \cosh 3\theta = 0;$$

hence, making $\frac{m^2 + n^2}{2mn} = \cosh 3\theta$ we have also $\frac{d^2}{2mn} = \cosh \theta$

The value of θ can be then found by aid of the tables of hyperbolic sines and cosines, compiled by the author, and published recently by the Society. The distance d can thus be determined in terms of m and n .

A method of finding the point experimentally is then described, and the distance between the poles ($2a$) shown to be given by the expression $\frac{a}{l} = \tanh \frac{3\theta}{2}$; where

$$\frac{l}{d} = \sqrt{\frac{\cosh 3\theta + 1}{4 \cosh \theta}}, l \text{ being the distance } oc. \text{ The}$$

latter function can be deduced from the tables already referred to.

Experiment shows that the distance between the virtual poles soon approaches the length of the magnet as d increases.

The strength of the field at P is given by the expression $\frac{4M}{d^3} \frac{\cosh^3 \theta}{4 \cosh^3 \theta - 1}$; where M is the moment of the magnet.

This can be simplified by arranging d and l so that $\cosh^2 \theta = \frac{5}{4}$, and then becomes $\frac{5M}{8d^3}$. Under these con-

ditions, $\frac{l}{d} = 0.85065$, and therefore the angle $oCP = 40^\circ 23' 10''$.

NOTICES OF BOOKS.

Decimal Coinage; Weights and Measures Popularly Explained. By Sir GUILFORD MOLESWORTH, K.C.I.B. and J. EMERSON DOWSON, M.Inst.C.E. Revised and issued by the Decimal Association, Eastcheap, E.C. Kenric B. Murray, Secretary.

It is, in these days, scarcely possible that any serious objection can be urged to the principle of decimal weights, measures, and coins. The object of the present pamphlet is to combat some of the objections to its introduction which are popularly entertained. Others, however, they overlook, and it might not be time lost were the Decimal Association to consider how these difficulties could be met or avoided. One of these points is the loss to be incurred by reducing all existing measures and weights to the condition of waste material, and by throwing aside all tables used by engineers, surveyors, &c. For this we can see no remedy: the loss must be faced sooner or later, and perhaps the sooner the better.

A second point concerns the law courts. It would be very easy for Parliament to legalise the metric system. But unless it is made universal and compulsory, it will merely increase the existing complication. Now, attempts at uniformity of weights and measures have hitherto been made with but slender success. The pound and the ounce are, indeed, the same throughout England, but the stone and the peck vary within distances of twenty miles. It will be necessary when we introduce the metric system to make it penal to sell, quote, or buy, by any of the old standards. Out of this, we fear, a popular election catchword would be manufactured against the Government which proposed the change.

A more tangible difficulty, but one capable of being

removed, lies in the names which the French and their followers have thought proper to give to the different metric denominations. These names are all polysyllabic, whilst the names of the majority of our customary weights and measures are monosyllables. Here, an improvement on the present guise of the metric system is possible. We might call, *e.g.*, the metre, *yard*, and the demi-kilogramme, *pound*; both, of course, being a little larger than the present weight and measure.

Another practical difficulty is the somewhat pedantic refusal of the friends of the metric system to make up their weights in any form other than in multiples and sub-multiples of 10. If we open a box of weights as used in the laboratory, we find the following pieces:—0.1, 0.2, 0.5, and 1.0. In an English set of grain weights the pieces are 1, 2, 3, 6, 10. Now on trial it will be found that the English arrangement allows us to make up any desired weight, on an average, with fewer pieces than does the French. Many persons also object to the flat pieces of metal with the value stamped upon them as being more open to mistakes than the bent wires used in English chemical weights. To prevent any confusion between, *e.g.*, 6 grains and 0.6 gm. the latter might be made of flattened wire.

These two latter points, of course, are mere matters of detail which fall within the competence of the makers of balances and weights. The nomenclature of the denominations seems certainly to merit the attention of the Association.

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—The penultimate paragraph of Mr. Friswell's letter in your last issue emphasises the urgency for the settlement of the controversy as to admission of persons to the Fellowship of the Chemical Society, for it is obvious that pending settlement either *all* or *no* candidates must be admitted.

It is therefore to be regretted that those taking part in the debate are discussing details rather than principles and imputing motives instead of ascertaining facts.

The issue is of the plainest:—

If the title F.C.S. be permitted to continue to confer, as it undoubtedly does, a distinct advantage on its possessor, causing him to be considered a chemist by the outside public, it is absolutely essential that none but perfectly qualified persons shall be allowed to hold it, and the most drastic employment of the ballot must be resorted to in order to check the admission of unqualified candidates, and means must be adopted to eject those who have already been admitted without due qualification.

If, on the other hand, the Chemical Society be merely a convenient common centre for all interested in chemistry, whether professional chemists or the veriest *dilettanti*, it is of the most urgent necessity that the pretensions of those using their membership for trade purposes shall forthwith be demolished by the wide and persistent advertisement of the fact that they have no qualification whatever, and that the letters F.C.S. are absolutely devoid of significance when used as a diploma. There appears to be no possible middle course.

Those responsible for the present agitation have adopted the first supposition as their working hypothesis, and are bestirring themselves to prevent future admission of those whom they consider unqualified, regardless of their illogical position in not crusading against those already admitted.

Those who do not agree with their views must needs

be anxious for the prompt execution of the alternative policy. Those upholding the present system (if any there be), accepting the public estimate of the high value of the title F.C.S., while bestowing it upon those who neither desire nor deserve to be considered chemists, convict themselves of being either illogical or dishonest.—We are, &c.,

A. G. BLOXAM.
BERTRAM BLOUNT.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—It is greatly to be regretted that Mr. Friswell should see fit to adopt the tone which he does in writing to you upon the above subject, and that in his no doubt well-meant anxiety for the welfare of the Society, he should be led into, what appears to me to be, an inaccuracy of statement. In your issue of 21st November, Mr. Friswell says that a circular recently issued by Messrs. Lloyd and Teed had "a remarkable resemblance in type and paper to Chemical Society's notices." This statement amongst others was denied by those gentlemen in your issue of 28th November, and with their opinion I concur.

Mr. Friswell now advances a fresh assumption with reference to the probable number of supporters of Messrs. Lloyd and Teed in so definite a manner that he must surely be in a position to prove the truth of this statement. Moreover, as his word is questioned, it becomes his duty, both to himself and the Society, to substantiate his facts and figures. If, on the other hand, Mr. Friswell should find that he has been misled into making an erroneous statement it would surely be in better taste to publicly withdraw his accusation, than to make a second statement which he asks your readers to believe without furnishing the least evidence in support.

It is clearly manifest that reform in the method of admission to the Chemical Society is needed in the interests of the profession, and equally obvious that a subject of such real importance should be calmly debated on its merits without the semblance of acrimonious insinuations or unpleasant personalities. These have no bearing on the issue.—I am, &c.,

W. J. LIVINGSTON.

18, Arbour Street, East Stepney.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 18, November 10, 1890.

New Researches on the Synthesis of Rubies.—E. Fremy and A. Verneuil.—The authors believed that they have solved the problem of "feeding" crystals of ruby in the dry way, just as other crystals are fed in the wet way. The crucibles are now heated by gas fires in place of coke. They often find amongst their red crystals others of a violet or a blue colour. They submitted to the Academy crystals red on one side and blue on the other. Hence, it appears probable that the colour of the ruby and the sapphire is due to one and the same metal—perhaps chrome in different stages of oxidation.

Compounds of Mercury Cyanide with Cadmium Salts.—Raoul Varet.—An account of cadmium-mercury iodide, bromide, and chloride.

The Fluor-Spar of Quincié.—H. Becquerel and H. Moissan.—Certain varieties of fluor-spar, if pounded, emit a peculiar odour. The spar from Quincié gives off gas of a penetrating scent, which recalls that of ozone and also that of fluorine. It decomposes water, forming hydrofluoric acid and ozonised oxygen. The authors conclude from their experiments that the fluor-spar of Quincié contains an occluded gas, which is observed escaping when the mineral is broken up under the lens. All the reactions of this fluor-spar may be simply explained by the presence of a small quantity of free fluorine among the occluded gases.

On the Analysis of the Hypophosphorous, Phosphorous, and Hypophosphoric Acids.—L. Amat.—The oxygen compounds of phosphorus may be distinguished from each other by their reductive power, *i.e.*, by the quantity of oxygen which they take up on their conversion into phosphoric acid. For this determination, there may be employed either mercuric chloride, as proposed and employed by H. Rose, or potassium permanganate. The former method is the more precise, but the more tedious.

Preparation and Properties of Benzoyl Fluoride.—E. Guenez.—Benzoyl fluoride is a colourless liquid, with an odour more irritating than that of benzoyl chloride. It boils at 145°, and burns easily, with a smoky flame edged with blue. It attacks glass with very great rapidity. The results of its analysis correspond with the theoretical composition of benzoyl fluoride.

Synthesis of Citric Acid.—A. Haller and M. Held.—The authors set out with the preparation of acetone-dicarboxylic ether, which they convert into cyanhydrin; this, again, is made to yield citric acid. The crystals obtained gave the form, the taste, and the general properties of the natural acid.

No. 20, November 17, 1890.

On the Name Bronze: New Indications.—M. Berthelot.—The author, in his *Introduction à la Chimie des Anciens*, expressed the opinion that the name "bronze" took its name from the town of Brundisium, the seat of certain manufactures in this alloy: *as Brundisium*. But in a manuscript three centuries older, discovered in the library of the canons of Lucca, and reprinted by Muratori in his *Antiquitates Italicae* we read: "De compositis brandisii: eramen partes II., plumbi parte I., stagni parte I." Another formula in the same work prescribes: "eramen partes II., plumbi partem I.; vitri dimidium et stagni dimidium. Commisceat at conflas; fundis; secundum mensuram vasorum facit et agluten eramenti cum asinitru." It is remarkable that the word *vitridum* in the exact meaning of vitriol is repeatedly found in this M.S., which shows that the word is much more ancient than the epoch of *Albertus Magnus*.

On the β -Pyrazol Dicarboxylic Acids.—M. Maquenne.—The author has formerly shown that dinitrotartaric acid reacts upon the methylic or ethylic aldehyds in presence of ammonia, giving rise to monobasic acids which heat splits up into carbonic acid and β -pyrazol (glyoxaline). The same reaction occurs with many other aldehyds, and nitrotartaric acid is a special reagent for these bodies.

On a Phenol-Acid Derived from Camphor.—P. Cazeneuve.—The author has obtained an acid, the amethylcamphophenol sulphuric, which precipitates quinine, chinchonine, brucine, and strychnine, but not morphine, from their saline solutions. When boiling it reduces gold and platinum chlorides and ammoniacal silver nitrate, the last more slowly. It precipitates gelatin, but not starch water. It precipitates baryta water, but not lime water. The tannins which are phenol acids behave in a similar manner.

On the Saponification of Halogenous Organic Compounds.—C. Chabré.—The author concluded that the alcohols of higher atomicity might be obtained by saponifying their fluorhydrines. He has applied this reaction successfully to ethylene fluoride.

On the Active Starchy Derivatives.—M. Philippe, A. Guye.—The author gives a table of forty amylic derivatives, which are all dextro-rotatory.

The Fixation of Gaseous Nitrogen by Leguminous Plants.—Th. Schloesing, Jun., and Em. Laurent.—The authors show by an indirect method of experimenting that nitrogen is really gained in the course of the vegetation of the legumens, and they prove by direct methods that this gain is really due to the fixation of gaseous nitrogen. M. Berthelot observed that this memoir seems to close the controversy relative to the fixation of free nitrogen by the joint action of the soil, and of plants under the influence of microbia.

On the Microbian of the Nodosities of Leguminous Plants.—Em. Laurent.—The organisms in question form a distinct group intermediate between the bacteria and the lower filamentous fungi. The author proposes to call them *Pasturiacae*.

No. 21, November 24, 1890.

Facts Relative to the History of Carbon.—Paul and Léon Schützenberger.—If a slow, regular current of pure, dry cyanogen is passed through a porcelain tube heated to cherry-redness, it is very imperfectly decomposed into carbon and nitrogen, the bulk of the cyanogen issuing from the tube unaltered. At a white red heat the decomposition is more active, and the inner surface of the tube becomes lined with a thin, bright, blackish grey layer, with a lustre resembling that of graphite. But if a long boat of retort-coke, dusted over with powdered cyclite, is placed in the hottest part of the tube, the decomposition of the cyanogen is complete, and the tube becomes ultimately stopped up with a deposit of blackish-grey elastic filaments matted together. If a fragment of aluminium is placed in the boat the carbon deposited in its neighbourhood is also filamentous, but devoid of elasticity, and assuming, after compression, the appearance of graphite. The filiform carbon formed by the pyrogenous decomposition of cyanogen in presence of vapours of cryolite is a peculiar variety of carbon, approximating to, but not identical with, electric graphite. The property of forming oxyhydrated derivatives capable of being suddenly destroyed by heat does not belong exclusively to graphites and is met with in certain varieties of amorphous carbon, such as retort-coke. It will therefore be suitable to abandon the too exclusive names of *graphitic acids* or *oxides*, and give these bodies the general name of carbon hydroxides.

On the Artificial Production of a Chrome Blue.—Jules Garnier.—The author melts together, in a lined crucible—Potassium chromate 48.64 grms.; fluor-spar 65.0 grms.; silica 157.0 grms. The product is a glass of a fine blue, surrounded with a thin layer of metallic chromium, which is capable of being detached. This process, it appears, had been deposited in a "sealed paper" on June 13, 1887.

Researches on the Application of Measurements of Rotary Power to the Determination of the Compounds Formed by Aqueous Solutions of Malic Acid, with Double Potassium, and Sodium Molybdate, and Acid Sodium Molybdate.—D. Gernez.—The author's results are given in the form of a table, which does not admit of abridgment.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iv., No. 2.

Applications of the Oleorefractometer of E. H. Amagat and F. Jean to the Detection of Sophistications.—Ferdinand Jean.—This instrument enables us to ascertain the purity of an oil by a simple reading. If the oil is falsified the deviation will be more or less removed from the special degree of the pure oil, and according as this deviation is increased or lessened, we have a datum bearing on the nature of the oil fraudulently added. The indications of the oleorefractometer should

always be controlled by determining the specific gravity and the thermic degree as shown in the thermoleometer. In this manner it is easy to detect margarine or similar matters to butter, and to distinguish pure butter from sophisticated butters. For the examination of butter and solid fats, such as tallow and lard, the oleorefractometer is regulated always with the same standard oil to the zero B of the scale, the adjustment and the observations being made at 45°. Under these conditions pure butters deviate -35°, whilst the margarine Mège-Mouries deviates only -15°. All the vegetable oils deviate strongly to the right, hence oleomargarines containing oils of sesame or cotton deviate still more strongly from pure butter. Pure lard gives a deflection of -12.5, and cotton oil +20°. Hence an addition of 5 per cent cotton oil is revealed by a decrease of 2.5° in the deviation of the lard. If the oleorefractometer is adjusted to a suitable standard it may be used for the examination of benzenes, petroleum, turpentine, methylenes, and essential oils.

Apparatus for Checking the Results in Sugar Works.—P. Horsin-Déon.—This paper requires the accompanying figure.

Action of Camphoric Anhydride upon Benzene in Presence of Aluminium Chloride. Formation of an Acid and Acetonic Compound.—E. Burcker.—By causing the above bodies to react under conditions very similar to those which give rise to benzoyl-propionic acids the author obtains a substance agreeing with the formula $C_{16}H_{20}O_3$, and possessing acid and acetonic properties. If separated from its sodium compound it forms very light crystalline laminae, soluble in absolute alcohol, ether, chloroform, and acetic acid, very sparingly soluble in benzene, and nearly absolutely insoluble in water. This substance melts at 125–126°, and does not resume the crystalline state if the melting point has been slightly exceeded.

New Apparatus for the Manufacture of Pure Yeast.—A. Feuerbach.—This paper requires the accompanying cut.

Separation and Determination of Zinc in Presence of Iron and Manganese.—J. Riban.—This paper will be inserted in full.

New Method for Measuring the Sugar to be used in Wines intended to become Effervescent with a Pressure of n Atmospheres without fear of Breakage.—E. J. Maumené.—The weight of normal sugar candy necessary to produce a given weight of carbonic acid is exactly known. It is therefore sufficient to weigh exactly the carbonic acid absorbed by the wine in question to produce a force of 5 or 6 atmospheres perfectly constant. When the equilibrium is obtained it is easy to weigh the carbonic acid if the wine has been weighed previously, and weighed again after the absorption. The difference gives the weight of the carbonic acid if this gas is perfectly pure and anhydrous.

Vol. iv., No. 3.

On the Dissociation of Selenium Tetrachloride.—C. Chabré.—The author, in opposition to W. Ramsay, maintains his former view that selenium tetrachloride is dissociated into chlorine and subchloride, which recombine in the cooler parts of the receiver.

Means of Obtaining Nitrogen Hydride, NH_3 .—E. J. Maumené.—The author heats the double chloride of platinum and ammonium in a glass retort fitted with a tubulure drawn out to a point and melted. The vapours are first directed into a small bottle, where they traverse the surface of a known weight of water, then through a tube containing a little potassa, and lastly into a trough of water. The properties of the compound will be described in a future communication.

Remarks on the Phenomenon of Coagulation.—A. Béchamp.—The author summarises the various meanings which chemists have given to the word "coagulation,"

and traces the history of the albumenoids of white of egg. Passing to the study of the albumenoids of milk he concludes that the isolation of caseine by acetic acid is a phenomenon of displacement and not a true coagulation.

Revue Universelle des Mines et de la Metallurgie.
Vol. x., No. 3.

Discovery of a Deposit of Uranium in Cornwall.—From the *CHEMICAL NEWS*.

Vol. xi., No. 1.

Chemical Industry at the Paris Exhibition of 1889. J. Krutwig.—A general review of the articles displayed at this exposition, which, of course, was the less interesting as one country exceptionally eminent in some departments of chemical industry declined to recognise the demonstration. The author still hopes for the success of artificial indigo, which he considers would be a great benefit.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 56.

Report Presented by M. H. Le Chatelier on Behalf of the Committee of Chemical Arts on a Memoir by M. Deval, Relating to the Assay of Cement and Hydraulic Lime with Hot Water.—Trials of resistance in cold throw no light on the quality of a cement, since cements with an excess of lime, which is certainly detestable, resist the ordinary trials perfectly. Portland cements of good quality made up into mortar with one-third of normal sand, resist hot water at 80°. They give, after 2 and 7 days of hardening in hot water, resistances equal to what they give with cold water at the end of 7 and 28 days. Cements which contain too great an excess of free lime, whether from defective burning or from wrong proportions, do not resist immersion in hot water after setting for 24 hours. When the excess of lime is less the briquettes may resist hot water after setting for a longer or shorter time. But in this case the resistances in heat at the end of 2 and 7 days are much greater than those obtained in the cold after 7 and 28 days. A comparison of the resistances in heat and cold enables us to recognise the presence of free lime in cements. The author recommends that the trials should be made by immersing the briquettes in water at 80°, twenty-four hours after they have been made.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xxi., No. 12.

Recognition and Determination of Starch.—A. Leclerc.—Starch may be dissolved out from other proximate vegetable principles, such as cellulose, fatty and nitrogenous principles, by means of neutral zinc chloride.

Detection of Olive-Kernels in Pepper.—M. Pabst.—Already noticed.

Determination of Urea.—D. B. Dott.—From the *Pharmaceutical Journal*.

Volumetric Determination of Emetine.—Blunt.—From the *Pharmaceutical Journal*.

The Oxidising and Decolourising Properties of Animal Charcoal.—P. Cazeneuve.—From the *Comptes Rendus*.

Preparation of Hydrobromic Acid.—A. Recoura.

Apparatus for Liquefying Chlorine.—B. Wilcox.—British Patent, 1888, No. 13070.

Electrolytic Preparation of Zinc and Tin.—M. Burghardt.—The process depends on the electrolytic decomposition of the solution of an alkaline sinkate or stannate.

Detection and Separation of Sodium and Lithium.—J. W. Thomson.—From the *Pharmaceutical Journal*.

Mineralogical Syntheses.—W. Bruhns.—From the *Bulletin de la Soc. Chimique*.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iv., Part 1.

The Colorimetric Determination of Nitric Acid by Means of a Sulphuric Solution of Diphenylamine.—J. A. Müller (From the *Bulletin de la Société Chimique*).

On the Attack of Certain Sulphides, such as Bournonite, Red Silver, &c., with a Current of Air charged with Vapours of Bromine.—P. Jannasch (*Journal für Praktische Chemie*).—Already inserted.

The Attack of Pyrites by a Current of Oxygen.—P. Jannasch (*Journal für Praktische Chemie*).—Already noticed.

Analysis of Wax.—H. Rättger.—The author concludes that in the analysis of bleached wax there is no need to adapt other normal numbers than for the analysis of yellow wax.

New Process for Utilising the Oxygen of the Air.—M. Georges Kassner.—The author has sought to substitute for barium manganate a body whose oxidising action may be as energetic as that of the manganate, which may be exerted under all circumstances, and which may be of an easy preparation. He has fixed upon calcium plumbate.

Use of Glycerin for Preserving Solutions of Sulphuretted Hydrogen.—From the *CHEMICAL NEWS*.

Improved Method of Obtaining Fine Crystallisations.—H. N. Warren.—From the *CHEMICAL NEWS*.

Preparation of Chlorine and Oxygen in the Cold in the State of a Continuous Current by means of Kipp's Apparatus.—Some time ago C. Winkler recommended for preparing chlorine in the cold a mixture of calcium hypochlorite and gypsum cast in sticks; these sticks when solidified are introduced into a Kipp's apparatus and treated with dilute hydrochloric acid, which produces a regular escape of chlorine at the common temperature. This process has been improved by R. J. Thiele, who simply submits the chloride of lime to energetic compression by means of a screw press so as to form a flat cake which is broken into fragments which are sufficiently resistant not to be liquefied in Kipp's apparatus. The only inconvenience of this method is that the chlorine may contain a little carbon dioxide, but in most cases this impurity has but slight importance. According to Volhard oxygen may be obtained with the same apparatus by causing oxygenated water to act upon the hypochlorite prepared as above described.

Rules for the Preservation of Antiquities.—From *Dingler's Journal*.

Conditions of the Reaction between Copper and Nitric Acid.—H. V. Riley.—From the *Journal of the Society of Chemical Industry*.

MISCELLANEOUS.

Royal Institution of Great Britain.—The following are the probable arrangements for the Friday Evening Meetings before Easter, 1891:—

Jan. 23rd. The Right Hon. Lord Rayleigh, M.A., D.C.L., LL.D., F.R.S. "Some Applications of Photography."

Jan. 30th. The Right Hon. Sir Edward Fry, Lord Justice, F.R.S., F.S.A., F.L.S. "British Mosses."

Feb. 6th. Professor J. W. Judd, F.R.S., F.G.S. "The Rejuvenescence of Crystals."

Feb. 13th. Professor A. Schuster, Ph.D., F.R.S., F.R.A.S. "Some Results of Recent Electric Experiments."

Feb. 20. The Right Hon. Lord Kelvin, M.D., F.R.S. "Infectious Diseases, their Nature, Cause, and Mode of Spread."

Feb. 27th. Percy Fitzgerald, Esq., M.A., F.S.A. "The Art of Acting."

March 6th. Professor J. A. Fleming, M.A., D.Sc. "Electromagnetic Repulsion."

March 13th. Felix Semon, M.D., F.R.C.P. "The Culture of the Singing Voice."

March 20th. Professor W. E. Ayrton, F.R.S. "Electric Meters, Motors, and Money Matters."

The Smoke Nuisance.—Meeting at St. James's Hall.—A well attended meeting was held at St. James's Hall on December 5th under the auspices of the Balloon Society of England. A well thought out and interesting paper was read by Mr. I. MacIntyre, B.A., upon the "Smoke Nuisance and its Solution." This was followed by a very vigorous discussion, the claims of many inventions being advocated. A resolution was ultimately put to the meeting and carried. "That the latest inventions for dealing with the difficulty, viz., Elliott's Smoke Annihilator, now being exhibited on the Thames Embankment, is worthy of the greatest consideration, and that the Government and the County Council be earnestly solicited to give a trial to the same."

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Society of Arts, 8. (Cantor Lectures). "Gaseous Illuminants," by Prof. Vivian B. Lewes.

Medical, 8.30.
TUESDAY, 16th.—Institute of Civil Engineers, 8.
Pathological, 8.30.

WEDNESDAY, 17th.—Society of Arts, 8. "Impressionism in Photography," by George Davison.

Metereological, 7.
Geological, 8.

THURSDAY, 18th.—Chemical, 8. "The Constitution of Hydracetic Acid," by Dr. N. Collie. "The Theory of Dissociation into Ions, and its Consequences," by S. U. Pickering. "Phennoic Acid," by Dr. A. Colefax.

Royal, 4.30.
Royal Society Club, 6.30.
FRIDAY, 19th.—Quekett Club, 8.

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THE CHEMICAL NEWS.

VOL. LXII. No. 1621.

LATEST RESEARCHES ON THE PHOTOGRAPHY OF METALLIC SPECTRA.*

By Prof. V. SCHUMANN.

I HAVE succeeded in photographing the ultra-violet spectrum beyond 1820 for a considerable extent. I thus obtain photographs which, if measured from Al No. 32, λ 1852 (Cornu), are two or three times as long as the entire spectral region between H (λ 4861) and Al No. 32. Hydrogen possesses the greatest photographic energy and the most refrangible rays; no other spectrum is so rich as this in lines in the extreme ultra-violet. These photographs can be taken only in a vacuum, and with plates sensitive for the ultra-violet. All known photographic plates, even the gelatin emulsion plates, are not sensitive for waves of very small wave lengths; hence they could, hitherto, not be photographed. I have invented a new sensitive plate the photographic maximum of which lies in the most refrangible spectral region. I propose, subsequently, to publish my process of preparing these plates.

During the last six weeks I have been perfecting my vacuum spectrograph, and have fitted it with a sliding slit which is within the apparatus, and consequently in a vacuum, but capable of being manipulated from without. For this purpose the slide is provided with two micrometers, one for the width of the slit and the other for its length. The edges of the slit are absolute edges, and the jaws are ground optically plane. These jaws are made of hard steel. I thus obtain a very even slit for the light, and consequently very well-defined spectrograms. When I use a magnifying power of 100^x the photographs taken are still fit for measurement. This is scarcely possible with other spectrograms on gelatin plates if strong magnifying powers are used.

I will shortly send you a sketch of the newly discovered lines of thallium, which lie beyond the lines shown in the spectrogram which I have already sent you. The taking of the photographs of these new lines involved especial difficulties, as the vapours of thallium oxide arising from the passage of the spark between the metallic electrodes coated the window of the vacuum spectrograph, and rendered it opaque, thus keeping back the effective rays. The air is so impervious to the most refrangible rays that I had to let the spark strike across quite close to the window. Hydrogen is very pervious, but the photographic energy of the spark striking in this gas is so faint that less can be done in this manner than in atmospheric air. Had the photographic action of the light been greater I should have allowed the spark to pass in hydrogen gas.

THE ANALYSIS OF WATER TO DETERMINE SCALE-FORMING INGREDIENTS.†

By Prof. THOMAS B. STILLMAN.

THE scale-forming ingredients of a water are usually composed of calcium and magnesium carbonates and calcium sulphate, and though an analysis of a water for boiler purposes usually states the number of grains per gallon of the above constituents, the analysis should also comprise the determination of many other ingredients, not

scale forming, that are necessary to a proper estimation of the former.

This is especially true of the alkalis, which are not always determined in a commercial analysis for boiler purposes, the amount of lime, magnesia, chlorine, carbonic and sulphuric acids being considered a sufficient index of the character of the water.

The alkalis and their salts rarely form scale in boilers,* and so cannot be classed as scale forming, yet they play fully as important a part in the relation they sustain to the sulphuric acid and chlorine.

If all the sulphuric acid in a water were combined with the alkalis there would be no sulphate of lime present, and the latter would be eliminated as part of the scale ingredients. This is a condition rarely occurring, however, since in most waters a portion of the sulphuric acid is united with the alkaline earths and the alkalis. The indirect estimation of the carbonic acid would be changed also. That is to say, where the CO_2 is estimated by uniting all the CaO and MgO (left uncombined with the SO_3 and Cl) with CO_2 , it is evident that if all the SO_3 is united with CaO , when a large portion belonged to the alkalis, the amount of carbonate of lime would be too small, and also that the proportion of the CO_2 would be deficient by the amount required to saturate the CaO incorrectly united with the SO_3 .

There is nothing in the usual commercial analysis to indicate whether the sulphuric acid, as determined in the water, is all united with the lime to form calcium sulphate or not; but the custom has been so to unite it; with the result that calcium sulphate may be represented as a large component of the scale-forming material, when in reality none whatever may be present. The converse is also true. In a partial analysis of the Monongahela River water (*Transactions American Institute of Mining Engineers*, vol. xvii., page 353), the amounts of objectionable substances, for boiler use, are given as follows:—

	Parts per 100,000.	Grains per gallon.
Total lime	161	= 94
„ magnesia	33	= 19
Sulphuric acid	210	= 122
Chlorine	38	= 22

It states further the amounts of carbonates of lime and magnesia precipitated upon boiling to be:—

	Parts per 100,000.	Grains per gallon.
Carbonate of lime	130	= 76
„ magnesia	21	= 12.2

The alkalis not having been determined, the proportion of sulphuric acid combined with lime becomes problematical; in fact, the inference is that there is none present, when, in all probability, it amounts to a large percentage.

Another example ("Report State Geologist," New Jersey, 1885, page 121), is as follows:—

Analysis of Water from Well No. 1.

	Grains per gallon.
Chlorine, as chlorides	2.2422
Sulphuric acid, as sulphates ..	0.3666
Silica	0.9098
Iron and alumina	0.0233
Lime	2.1461
Magnesia	0.3965

Alkalies and undetermined matter ..	6.0845
	6.7155

Total solids 12.800

* A sample of scale, analysed by the author in 1887, had the following composition:—Carbon, 1.01; SiO_2 , 1.38; Al_2O_3 , 0.43; NaCl , 7.12; KCl , 1.01; MgCl , 1.71; CaCl_2 , 10.32; CaSO_4 , 11.20; Undetermined, 0.68; Total, 100.00.

* Extracts from letters to the Editor.

† The *Stevens Indicator*, vol. vii., No. 4, Oct., 1890.

Analysis of Water from Well No. 2.

	Grains per gallon.
Chlorine, as chlorides	1'1955
Sulphuric acid, as sulphates ..	0'3091
Silica	0'5948
Iron and alumina	0'0233
Lime	3'7907
Magnesia	0'6531
	6'5665
Alkalies and undetermined matter ..	5'5519
Total solids	12'1184

Numerous instances are constantly being cited in the literature of technical water analyses of similar incomplete analyses, and having thus indicated the necessity of including the alkalies, the accompanying scheme has been arranged to show the method of making a water analysis for boiler purposes.

To show in detail the method of using the scheme, the following water analysis is given. (Preliminary tests having shown the water to contain but little residue, 8 litres of it were evaporated).

	Grms.
Pt capsule and residue (8 litres)	147'460
" without residue	146'620
Total residue	0'840
Before ignition, capsule and residue	147'460
After " " " "	147'197
Organic, volatile (CO ₂ , &c.)	0'263
SiO ₂ + crucible	15'970
Crucible	15'904
SiO ₂	0'066
Solution made to 100 c.c.—75 c.c. for bases, 25 c.c. for SO ₃ .	
75 c.c.	
Fe ₂ O ₃ (Al ₂ O ₃) + crucible	15'9338
Crucible	15'903
	0'0308
CaO + crucible	16'0197
Crucible	15'903
CaO	0'1167
MgO + crucible	15'928
Crucible	15'903
MgO	0'025
SO ₃ .	
Crucible and BaSO ₄	16'023
Crucible	15'903
BaSO ₄	0'120

The chloride found by titration amounted to 0'0055 grms. per litre, or 0'32 grain per gallon.

	Grms.
Pt dish and alkaline sulphates and (MgSO ₄)	53'370
Pt dish	53'197
Sulphates	0'173

Dissolved in H₂O, made solution up to 50 c.c.—25 c.c. for magnesia determination, and 25 c.c. for potash determination.

	Grms.
Mg ₂ P ₂ O ₇ + crucible	15'942
Crucible	15'904
Mg ₂ P ₂ O ₇	0'038
0'038 × 2 = 0'076 Mg ₂ P ₂ O ₇	
Mg ₂ P ₂ O ₇ : (MgSO ₄) ₂ :: 0'076 : × MgSO ₄ = 0'082 gm.	
K ₂ Cl ₃ Pt Cl ₄ , on tared filters = 0'023 gm. corresponds to 0'0046 K ₂ SO ₄ in the 50 c.c.	

Having determined the amounts of sulphates of magnesium and potassium, the residue remaining is sulphate of sodium, as follows:—

	Grm.
Total sulphates	0'173
Magnesium sulphate	0'082
Sulphates of sodium and potassium ..	0'091
Sulphate of potassium	0'0046
Sulphate of sodium	0'0864

And calculated to their oxides would be as follows:—

	Grm. for 75 c.c.	Grm. for 8 litres.
MgO	0'027	0'036
Na ₂ O	0'0377	0'0502
K ₂ O	0'0025	0'0034

The weights above obtained are calculated in terms of the total residue, 8 litres, and then converted into values corresponding to 1 litre, the result being as follows:—

	Grm. per litre.
Silica	0'0082
SO ₃	0'0206
Cl	0'0055
K ₂ O	0'0005
Na ₂ O	0'0062
MgO	0'0077
CaO	0'0194
Fe ₂ O ₃ (Al ₂ O ₃)	0'0051
Organic, &c.	0'0193
Carbonic acid	0'0137
Oxygen in excess of Cl.	0'0016
Total residue	0'1046
(To be continued).	

THE DRY ASSAY OF TIN ORES.*

PART II.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.
(Continued from p. 293).

(3). THE mica used was a pure white muscovite.

The general behaviour of the assays, according to the German method, Nos. 132 to 136 (see Table XXIV.), is the same as those with felspar, the exception being that with 50 per cent of mica only an incomplete fusion could be obtained. In the bottom of the crucible was a porous fritted dark mass, no tin being visible; it was covered by a semi-fused scoriaceous spongy mass of a brown colour. The buttons had the same appearance and properties as those from the felspar mixture. The results show a greater loss of tin and a stronger reduction of iron than above, the reason being that muscovite is more refractory in the assay than albite.

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. III., No. 3.

TABLE XXIV.

No. of assay.	Charge.							Resulting tin.		Resulting alloy.	
	Ore. Grms.	Muscovite.		Char. coal. Grm.	Bl. flux substitute. Grms.	Borax glass. Grms.	Potass. cyanide. Grms.				
		Grms.	Per cent.					Grms.	Per cent.	Grms.	Per cent.
132.	5	1	16.66	1	18	1	—	—	—	3.190	63.80
133.	5	2	28.57	1	21	1	—	—	—	3.250	65.00
134.	5	3	37.50	1	24	1.5	—	—	—	3.200	64.00
135.	5	4	44.44	1	27	1.5	—	—	—	3.605	72.10
136.	5	5	50.00	1	30	2	—	—	—	—	—
137.	5	1	16.66	—	—	—	24	3.260	65.20	—	—
138.	5	2	28.57	—	—	—	28	3.235	64.70	—	—
139.	5	3	37.50	—	—	—	32	3.165	63.30	—	—

TABLE XXV.

No. of assay.	Charge.						Resulting tin.		Resulting alloy.		
	Ore. Grms.	Tourmaline.		Char- coal. Grm.	Bl. flux substitute. Grms.	Borax glass. Grms.	Potass. cyanide. Grms.	Grms.	Per cent.	Grms.	Per cent.
		Grms.	Per cent.								
140.	5	1	16.66	1	18	1	—	—	—	3'470	69.40
141.	5	2	28.57	1	21	1	—	—	—	3'300	66.00
142.	5	3	37.50	1	24	1.5	—	—	—	3'250	65.00
143.	5	4	44.44	1	27	1.5	—	—	—	2'295	45.90
144.	5	5	50.00	1	30	2	—	—	—	—	—
145.	5	1	16.66	—	—	—	24	3.285	65.70	—	—
146.	5	2	28.57	—	—	—	28	3.250	65.00	—	—
147.	5	3	37.50	—	—	—	32	3.235	64.70	—	—

TABLE XXVI.

No. of assay.	Charge.							Resulting alloy.	
	Ore. Grms.	Garnet.		Char. coal. Grm.	Bl. flux substitute. Grms.	Borax glass. Grms.	Potash. cyanide. Grms.		
		Grms.	Per cent.					Grms.	Per cent.
148.	5	1	16.66	1	18	—	—	3.685	73.70
149.	5	2	28.57	1	21	—	—	3.720	74.40
150.	5	3	37.50	1	24	—	—	3.695	73.90
151.	5	4	44.44	1	27	—	—	3.930	78.60
152.	5	5	50.00	1	30	—	—	4.125	82.50
153.	5	1	16.66	—	—	—	24	3.365	67.30
154.	5	2	28.57	—	—	—	28	3.435	68.70
155.	5	3	37.50	—	—	—	32	3.490	69.89

TABLE XXVII.

No. of assay.	Charge.						Resulting tin.		Resulting alloy.		
	Ore. Grms.	Columbite.		Char. coal. Grm.	Bl. flux substitute. Grms.	Borax glass. Grms.					Potass. cyanide. Grms.
		Grms.	Per cent.				Grms.	Grms.	Grms.	Grms.	
156.	5	1	16.66	1	18	1	—	—	—	3.400	68.00
157.	5	2	28.57	1	21	1	—	—	—	3.605	72.10
158.	5	3	37.50	1	24	1.5	—	—	—	3.775	75.50
159.	5	4	44.44	1	27	1.5	—	—	—	3.820	76.40
160.	5	5	50.00	1	30	2	—	—	—	3.875	77.50
161.	5	1	16.66	—	—	—	24	3.355	67.10	—	—
162.	5	2	28.57	—	—	—	28	3.370	67.40	—	—
163.	5	3	37.50	—	—	—	32	3.300	66.00	—	—

In the assays with potassium cyanide, Nos. 137 to 139, the behaviour of mica is similar to that of felspar, the mica appearing also here more refractory.

(4). The tourmaline pulverised for the experiments was the large black crystal which occurs so often with the tin ore.

In the German method, Nos. 140 to 144 (Table XXV.), the upper slag is parrot-green, the lower slag is slightly vitreous, but quickly becomes stoney with the increase of tourmaline. The buttons have all a grey surface; they dull, brittle, hard to cut, and ferruginous. These properties increase with the addition of tourmaline. In assay No. 124 no complete fusion could be obtained, and no button or particles of alloy were visible in the porous fritted dark mass. The results show a loss of tin increasing

with the addition of tourmaline, and an increased amount of iron is taken up by the tin.

With potassium cyanide, tourmaline has no effect that is essentially different from that of previous assays, as the slags show about the same appearance, and the buttons the same properties and nearly the same weight.

(5). The garnet occurring in the tin deposits is the iron garnet (almandite). It has a brownish red to fine deep red colour, and is very rich in iron. This appears in its high specific gravity, 4.149, and from the fact that, after being heated by itself in a crucible to a bright red heat, it shows magnetic properties. For the experiments, transparent crystals of a fine deep red colour were pulverised.

From Table XXVI. it will be seen that no borax was added to the charges of the German assay, Nos. 148 to 152,

as the garnet with the addition of a small amount of base (lime or alkali) forms a liquid slag. The salt slags were less crystalline than usual, but otherwise the same with the exception of the colour, which varied from light to dark red. The borax slags lost their vitreous and brittle character by the addition of garnet, became stony and tough, and changed from subtranslucent to opaque. The colour, a dull olive-green, became lighter, the last slag, No. 152, being peacock-green. The buttons were all a dull dark grey, hard to cut, brittle, and rich in iron. The weights obtained in the first four assays, Nos. 148 to 151, are strikingly close. This would seem to show that about the same amount of iron had been present in all of them, forming an alloy of nearly the same composition, the rest of the iron having remained in the slag. The uniformly well melted charges, and the beautiful manner in which the one-button separates from the slag above, show that, if tin is to be recovered from siliceous ore as an alloy, a basic silicate of iron is the best, because it gives up the necessary iron for the tin and also retains sufficient in combination to form with the alkali of the charge a readily fusible brittle slag.

In the cyanide assays the compact white upper slag decreases, and the porous bluish green lower slag increases as garnet is added to the charge. In No. 153 (Table XXVI.) the proportions were half and half, in No. 155 one quarter white and three quarters grey. The buttons are all ferruginous and show the usual characteristics. The figures prove that, although iron has been taken up, tin has gone into the slag.

(6). The columbite found with the tin ores has an iron-black colour and a streak that varies from a very dark brown to a pure black. The pure mineral has the following composition:—

	Per cent.
Ta ₂ O ₅	18.20
Nb ₂ O ₅	64.09
FeO	11.21
MnO	7.07
SnO ₂	0.10
CaO	0.21
Total	100.88

The specific gravity varies between 5.89 and 6.12. The columbite used for the experiments contained a small proportion of albite.

In the German assays, Nos. 156 to 160 (Table XXVII.), the salt slags were stony and dull; their colour, at first, a brownish green, gradually lost the brown, and became finally parrot-green. The borax slags were vitreous, brittle, and had a resinous lustre, the colour changing from a light to a dark olive-green. The buttons were all ferruginous; their colour, at first a dark grey, became black. The results show that the amount of iron reduced increased with the percentage of columbite added to the charge. Also, that if tin ore containing columbite be treated on a large scale, the columbite will probably behave in a way similar to the wolframite of Cornwall ores, where the iron that alloys with the tin is the principal cause of trouble, and not the tungsten of the mineral which, according to Berthier,† may be present in considerable quantities.

In the experiments with potassium cyanide the upper slags showed the usual properties, the lower slags were very porous, slightly glassy, and had a dark blue-grey colour. The porosity increased with the percentage of columbite added. The buttons were white, bright, malleable, easily cut, and contained very little iron; from their appearance they might have been supposed to be free from iron, until especially examined for this metal. If pure cassiterite and pure columbite are ground together and fused, thus intimately mixed, with potassium cyanide, the iron and manganese of the columbite combine with

the tin, leaving a yellowish slag which contains the columbic and tantallic acids.*

By comparing the effect produced by the associated minerals in the two methods of assay, we see that the cyanide assay must be accorded the preference, although, if the amount of associated mineral be small, the German method will give entirely satisfactory results.

In concentration works, where several assays have to be made daily, the question of cost must be considered, and the cheap German assay will probably be preferred to the more expensive one, especially if the assay is only made in order that the manager may know how pure his concentrates are. In questions connected with the buying and selling of ores or concentrates, the assay with potassium cyanide is better, because the associated minerals have comparatively little influence on it.

(To be continued).

THE COEFFICIENT OF MINERAL CONDENSATION IN CHEMISTRY.†

By T. STERRY HUNT.

1. THAT the solid and liquid mineral species known to us (including under the designation of minerals all distinct forms of unorganised matter) are formed by a process of intrinsic condensation or so-called polymerisation from simpler chemical species, which are themselves often gaseous, and, moreover, that this condensation is very considerable, is a conclusion to which chemists have been naturally led. The problem of fixing its amount, or, in other words, of determining the coefficient of the condensation which results in the production of such mineral species, is one which must present itself to every earnest student of chemical physics, but has nevertheless hitherto been generally disregarded. A reason for this neglect of the problem is to be found in the belief that it does not admit of solution, as may be shown by citations from the writings of many eminent chemists.

2. Thus Wolcott Gibbs in 1877, after reviewing the researches of his predecessors, Marignac, Scheibler, H. Deville, and Debray, on the various polytungstates and polymolybdates, and his own important contributions to the subject, describes these various bodies as salts of "complex inorganic acids," and proceeds to illustrate by formulae, the results of their chemical analysis. Of a certain hydrated phosphovanadotungstate of barium examined by him he declares that "it has the highest molecular weight yet observed, 20,058." By this we are to understand no more than that this number corresponds to the simplest chemical formula admissible, for he further says, "We have no positive knowledge of the composition of these salts, their molecular weights being, as in the case of most inorganic compounds, entirely unknown," adding that research "tends constantly to show that the structure of inorganic bodies is more complex than was formerly supposed."‡ The language of Roscoe in 1884 embodies the same thought when he speaks of looking forward to "the establishment of a systematic inorganic chemistry which need not fear comparison with the organic branch of our science"; and adds, referring to the complex inorganic acids of Gibbs: "It is well to be reminded that complexity of constitution is not the sole prerogative of the carbon compounds, and that before this systematisation of inorganic chemistry can be effected we shall have to come to terms with many compounds concerning whose composition we are as yet wholly in ignorance."§ It may be remarked, in passing, that the

* Drs. Carpenter and Headen, *Trans. Am. Inst. Mining Engineers*, vol. xvii., p. 533.

† From the *American Chemical Journal* for November, 1890, vol. xii., No. 8.

‡ Gibbs, "Complex Inorganic Acids," *Am. J. Sci.* (3), xiv., 61.

§ Roscoe, Address to the Chemical Section of the Brit. Assoc. Adv. Science, at Montreal in 1884; Report, p. 663.

* *Trans. Am. Inst. Mining Engineers*, vol. xvii., p. 593.

† "Taité des Essais," 1847, vol. ii., p. 472.

retention by these writers of the old antithesis between organic and inorganic chemistry, as distinguishing carbonaceous compounds from other species, can only serve to hinder the systematisation and the unification of the facts of the science.

Still more recently, in 1889, Victor Meyer, in his address before the Association of German Naturalists and Physicians at Heidelberg on "The Chemical Problems of To-day," says with regard to the question of intrinsic condensation: "We know to-day very well that the silicon oxide cannot have the formula SiO_2 , and that this must be multiplied by a very large factor, but of the numerical value of this last we have no indication." Further he adds: "We lack the least knowledge in regard to the true molecular weight of minerals."*

3. The direct and concise language of Louis Henry of Louvain, in 1879, may be taken as a fuller expression of the opinions generally entertained by chemists on this subject up to the present time. Having shown that for most oxides of the elements the normal forms corresponding with the chlorides, as in the case of iron, aluminium, titanium, silicon, &c., are unknown, and that we possess only greatly condensed polymers of these oxides $(\text{RO}_x)_n$, he proceeds to inquire: "What is the true value of n , the coefficient of polymerisation, or, in other words, what is the real molecular formula of these polymeric oxides? These questions are, doubtless, of great interest, but it should be stated at once that it is absolutely impossible to give a direct answer. I do not know of any fact which would allow us to assign an absolute value to the coefficient of polymerisation, n So far as facts will permit a conclusion, we may affirm that in most cases this number is very high, though different for different oxides."†

4. The same important questions had been propounded by the present writer in 1853, when, after noting that the equivalent weights for volatile bodies are known from the densities of their vapour, but in the case of non-volatile bodies are assumed, it was said that "having determined the true equivalent of a species from the density of its vapour, the inquiry arises whether a definite and constant relation may not be discovered between its vapour-density and the specific gravity of a species in its solid state. Such a relation being established, and the value of the condensation in passing from a gaseous to a solid state being known, the equivalents of solids, like those of vapours, might be determined from their specific gravities." The question was then asked, "What is the value of the condensation which takes place in the change from the gaseous to the solid state? or, in other words, what equivalent corresponds to a given specific gravity in any crystalline solid?" It was further said: "The equivalent of a crystallised species may often be a multiple of that deduced from those chemical changes which commence only with the destruction of its crystalline individuality." This point was then illustrated by examples in the history of various soluble crystalline species.‡

5. The question thus proposed by the writer in 1853, and repeated by Louis Henry in 1879, was persistently kept in view by the writer, and discussed at intervals in many published papers until 1886, when he arrived at what he has elsewhere put forth as, in his opinion, a simple and natural solution. This is found in the conclusion that the volume, not only of gases and vapours, but of all

species, whether gaseous, liquid, or solid, is constant, and that the integral weight—being the so-called equivalent or molecular weight—varies directly as the density, for which he proposes as the unit that of hydrogen at the standard temperature and pressure of 0° and 760 m.m.

In all cases of polymerisation and depolymerisation of gases and vapour, or, in other words, of intrinsic condensation and intrinsic expansion at ordinary pressure, the law of volumes, so far as known, holds good; that is to say, these changes are subordinate to a simple ratio of volumes. This same law, it is here maintained, applies equally to the production of dense vapours of liquids under increased pressure at temperatures above their critical points. Such dense vapours are polymers, which, on reduction of temperature, pass into liquid or solid polymers; the law of condensation by volumes being, by the present hypothesis, assumed to be a universal one. The relations here indicated have been elsewhere considered at length, when, after discussing the law of volumes in ordinary cases of condensation or polymerisation, it was said: "All analogy leads us to extend this law to the still greater condensations observed in the dense vapours into which liquid species above their critical points are resolvable, and to the farther condensation of these vapours into liquid and solid forms—to assume, in fact, that the law of combination by volume, like that of combination by weight (with which, so far as experience shows, it is indissolubly linked), is universal."* If this assumption, which appears to be in accordance with all the facts known, be admitted, the great problem proposed, namely the fixing of the coefficients of condensation for liquid and solid species, though a complex one, is solved.

6. As a preliminary to a further treatment of this problem it here becomes important to note the relations between what (1) we have designated respectively as the "chemical species" and the "mineral species." This will, moreover, serve to explain the language used in 1853, and cited above in speaking of crystalline species, as to "those chemical changes which commence only with the destruction of crystalline individuality." We may, perhaps, best approach the subject by conceiving the characters of a given species to be imposed upon matter by a force which is the form of that species, and which makes it what it is. The permanence of what we recognise as elementary species, in opposition to the notion of their transmutability, is the foundation of our chemical science, and from this it follows that secondary forms are imposed upon these, and present an ascending series often passing through two or more chemical forms before receiving the mineral form, which may be in turn subordinated to some biotic form.

7. These relations may be illustrated by well-known chemical facts: acetic and formic aldehyds and their sulphur and chlorine derivatives present many instructive cases of polymerism available for our purpose. Thus acetaldehyd, itself a very light and volatile liquid, is readily transformed into a denser and less volatile species, paraldehyd, which becomes a crystalline solid at 0° , melting at 10° , and having a vapour-density equal to $3(\text{C}_2\text{H}_4\text{O})$, or three times that of the normal aldehyd, into which, however, it is easily changed. The same aldehyd also gives a less fusible crystalline polymer, metaldehyd, integral weight of which, from the facility with which it reverts without melting to the normal vaporous aldehyd is unknown. Again, formaldehyd is a gas soluble in water, from which by heat it is in part expelled and in part changed into a white, volatile, crystalline solid, insoluble in water, alcohol, or ether, melting at 152° , but passing at a lower temperature into a gas having the density of the normal formaldehyd. A similar change is

* *Deutsche Rundschau*, Nov., 1889; translated by L. H. Friedberg in the *J. Am. Chem. Soc.*, x1, 101.

† Louis Henry, "Études de Chimie Moléculaire," Part I; "Les Oxydes Métalliques," *Ann. Soc. Scient. Brux.*, 1879. A translation of this, by Prof. T. Carnelley, entitled "The Polymerisation of Metallic Oxides," appears in the *L. E. and D. Philos.*, May and August, 1885. See further the author's "New Basis for Chemistry," pp. 117–122; also *Ibid.*, 2d ed., p. 217, note.

‡ "The Theory of Chemical Changes and Equivalent Volumes," *Am. J. Sci.*, March, 1853 (xv, 226–234); also in *L. E. and D. Philos.* (4) v., 526; and in a German translation in the *Chem. Centralb.*, 1853 (p. 849). This paper is reprinted in the author's "Chem. and Geol. Essays" (1874), pp. 426–437. See also "A New Basis for Chemistry," Chap. IV.

* See "A New Basis for Chemistry" in several chapters, and further in chap. XIV. of the 2d ed. thereof. Also in an essay on "The Foundations of Chemistry," §15–19, *Am. Chem. Journ.*, x, 344, from which the above extract is taken, and *Chem. News*, lviii., 193, 205, 212.

also effected when it is heated with water under pressure to a temperature above 100° , the normal aldehyd being taken into solution. This insoluble body, which is sometimes called methylene-oxide, and yields another and a less fusible modification, has been regarded as $3(\text{CH}_2\text{O})$, but its integral weight is uncertain. When a solution of formaldehyd is digested with milk of lime it is changed into a sugar which has been named formose, represented by the general formula of the glucoses, $\text{C}_6\text{H}_{12}\text{O}_6 = 6(\text{CH}_2\text{O})$. Indeed, by modifying the conditions of experiment many species of sugar, alike non-fermentescible and fermentescible, are obtained from formic aldehyd. From one of the latter, which has been designated acrose, and is a form of levulose, it has been found possible to produce anhydrous crystalline dextrose, and thus from the formic aldehyd itself to effect the synthesis of dextrose.*

8. Other striking examples alike of isomerism and of polymerism are seen in many hydrocarbons, as in the terpenes in acetylene and amylene; while the higher olefines are all polymers and possible homologues of the as yet unknown methylene CH_2 . In the case of the terpenes proper we have a large number of distinct liquid and solid species differing alike in boiling point, in optical characteristics, and in various chemical relations, but having a common vapour-density corresponding to $\text{C}_{10}\text{H}_{16}$. These include (1) pinenes, which are liquids boiling at 156° – 160° and having a specific gravity of about 0.876 at 0° ; (2) citrenes; (3) sylvestrene; (4) terpine; all liquids boiling from 170° to 176° and with specific gravities very near that of the pinenes; while the (5) camphenes are solid crystalline species. The various pinenes and citrenes are in great part broken up by heat into pentine, C_5H_8 , which is again convertible into terpine. The various terpenes are, moreover, easily polymerised, yielding denser and less volatile liquids, including sesquiterpenes, $\text{C}_{15}\text{H}_{24}$, and still higher polymers boiling at 300° and upwards. Acetylene, C_2H_2 , under proper conditions of temperature, gives rise to a number of polymers, of which it suffices to mention benzene, $3(\text{C}_2\text{H}_2)$, cinnamene, $4(\text{C}_2\text{H}_2)$, itself a liquid passing into a solid modification), and retene, $9(\text{C}_2\text{H}_2)$, a crystalline solid. Of the higher olefines, at least three are known as solids at ordinary temperatures, namely, octadecylene, $18(\text{CH}_2)$, cerotene, $27(\text{CH}_2)$, and melene, $30(\text{CH}_2)$, having melting-points of from 18° to 62° and specific gravities of 0.79, 0.86, and 0.89, respectively, water being 1.00. The integral or so-called molecular weight of these various hydrocarbons is known by the density of their vapours, as in the similar cases of the chlorides of carbon, silicon, aluminium, and iron, and of the volatile oxides like those of carbon, arsenic, sulphur, selenium, ruthenium, and osmium.

9. By far the greater number of species, however, are either fixed at high temperatures or undergo heterogeneous decomposition thereby, and may be divided into two categories. First, those which are soluble in water or some other liquid, from which they can be recovered unaltered by change of temperature or by evaporation of the solvent. Such are the sugars and a vast number of non-volatile hydrocarbonaceous species, a great many chlorides, sulphates, phosphates, carbonates, and other salts, as also the elementary solid species, sulphur, phosphorus, and iodine. For these various bodies water, alcohol, ether, benzene, acetic acid, carbon disulphide, and other solvents are familiarly employed. In the second category is included the great number of species which are altogether insoluble, or else are either decomposed or enter into more or less stable combinations with their solvents. Such are the native silicates, oxides, carbonates, and sulphides among compounds, and the various metals among elementary species.

10. For these two categories of bodies it is obvious that the question of their integral or molecular weight must be approached by a wholly different process from that applied to volatile bodies. Much attention has of late been given

to the cryoscopic method of Raoult (with its modifications), which is applied for fixing this value for soluble non-volatile species, and depends upon the reduction of the temperature of congelation of the solvent which takes place after the solution therein of a known proportion of the solid species to be examined; the dissolving liquids chiefly used hitherto being water, acetic acid, and benzene. The results obtained are approximative, and, moreover, are extremely instructive as illustrations of the subject now under consideration. Thus, Tollens and Mayer have deduced thereby for formaldehyd (obtained in aqueous solution by effecting the transformation of the insoluble formic paraldehyd by heating it in a sealed tube with water to near 140°) the numbers 34 and 35, the calculated integral or molecular weight being $30(=\text{CH}_2\text{O})$. This solution, heated in a water-bath, regenerates the insoluble polymer, but evaporated over sulphuric acid gives a soft soluble solid which, by Raoult's method, is found to correspond to $2(\text{CH}_2\text{O})$. By applying this same method to dextrose, these observers found the number 188.7, the received formula for this and the other true glucoses being $\text{C}_6\text{H}_{12}\text{O}_6(=180)$; while arabinose and its isomer xylose, represented by $\text{C}_5\text{H}_{10}\text{O}_5(=150)$, give the numbers 155.1 and 154.1. For cane sugar and for lactose, which, with many other sugars, belong to the diglucosic type, designated as saccharose and represented by—



they found, by the method of Raoult, numbers which sustain this formula. For the sugar named raffinose, which occurs with saccharose in certain syrups, three formulæ, with C_6 , C_{12} , and C_{18} respectively, have been proposed. The latter, making it a triglucosic sugar, is $\text{C}_{18}\text{H}_{34}\text{O}_{16.5}\text{H}_2\text{O}(=594)$, and experiments by the cryoscopic method gave numbers from 544 to 644, thus sustaining the triglucosic character, and showing at the same time that the range of error due to the necessary imperfections of the process is not inconsiderable.

11. The recent application of this method to various uncrystalline amyloid bodies has given further results of great interest. The studies by many investigators of the hydrolysis of starch had already led to the conclusion that its constitution is far more complex than is indicated by the ancient formula $\text{C}_6\text{H}_{10}\text{O}_5$. The first action of cold dilute acids thereon changes it into the so-called soluble starch, which by hydrolysis is slowly converted into amyloextrine, with the production of a portion of dextrose. The action of diastase, in like manner, by successive stages in hydrolysis, gives rise to maltose and other forms of dextrine. By Raoult's method maltodextrine gives numbers closely approximating—



and amyloextrine,



inulin having a composition intermediate between the two. Raoult's method could not be applied to starch paste, but with soluble starch the depression in temperature produced, though slight, corresponded in a number of experiments to integral weights varying from 20,000 to 30,000. Messrs. Brown and Morris, to whom we owe these late investigations, are led to assign to soluble starch the formula $5(\text{C}_{12}\text{H}_{20}\text{O}_{10})_{20}(=32,400)$, thus multiplying the old empirical formula $\text{C}_6\text{H}_{10}\text{O}_5$ by 200. By the author's hypothesis, however, as re-stated in §5 of the present paper, the highest integral weights compatible with the observed specific gravities of starch and other amyloid bodies are approximately 32,000, and it therefore seems probable that the so-called soluble starch, which is apparently the first product of the depolymerisation of true starch, should be represented by some simple fraction, perhaps one-half the above, leading to an integral weight for soluble starch of 16,200. The above formula of Brown and Morris, equal to $200(\text{C}_6\text{H}_{10}\text{O}_5)$, will then represent starch itself, with an integral weight of 32,360 ($\text{O}=15.96$) and a theoretical specific gravity of 1.509. The recent examina-

* Fischer, *Ber. d. chem. Ges.*, xxiii., 372, cited in *Am. Chem. Journ.*, xii., 357–364.

tion by Sebanéeff of glycogen by Raoult's method leads to the formula $(C_6H_{10}O_5)_{10} (= 1620)$.

12. It will now be sufficiently evident that the values got by Raoult's method are not the integral or so-called molecular weights of the solid species themselves, or what we have designated *mineral species*, but of the *chemical species* which result from the depolymerisation of these, and which pass into solution. These values, moreover, bear no obvious relations to the specific gravities of these solid species, as appears when we compare sugars like xylose, dextrose, saccharose, and raffinose with each other, and with the dextrines and soluble starch; bodies which with such widely different integral weights in solution have almost identical specific gravities in the solid state. It is, in the language of the atomistic school, "the molecular mass" of the dissolved substance which we determine by Raoult's method, and not that of the solid or liquid mineral species, from the depolymerisation of which, in the process of solution, is derived the chemical species; the molecular or, in other words, the integral weight of which ($H=1$) may vary widely in bodies nearly allied, as in hydrocarbons of identical centesimal constitution, different sugars, and certain amyloid substances. The total mineral condensation in such cases being essentially the same, the question is whether the depolymerisation or homogeneous disintegration which takes place in vapourisation or in solution shall resolve the mineral species into a greater or less number of chemical species.

Chemical species probably never assume liquid or solid forms. They are either vapours or gases, which by intrinsic condensation (polymerisation) pass into liquids or solids, or else, if their integral weight is too great to permit their existence in a gaseous condition at ordinary temperatures, unite with water, forming liquid hydrates, from which they separate, after a longer or shorter time, in solid or, more rarely, in liquid hydrated or anhydrous species. The appearance of such solid or liquid bodies in the midst of an aqueous solution marks the passage of the dissolved *chemical species* by polymerisation into a *mineral species*: a process often favoured by mechanical agencies or by change of temperature.

13. The significance of these relations is made more apparent by the writer's theory of solution, according to which there are formed in the process of aqueous solution definite compounds of the dissolved matters with water, accompanied with all the phenomena of chemical union; the further addition of water thereto giving rise either to new chemical arrangements of the substances present, or to simple admixtures of one definite solution or liquid species with another of unlike density. Examples of such admixtures of aqueous solutions are seen in the case of phenol and water, which when heated mix in all proportions, but on cooling separate into two layers, the lower a solution of phenol in water, and the upper a solution of water in phenol. Aniline and many other bodies present similar reactions with water below $100^{\circ}C$, and like results are got through the agency of pressure at still higher temperatures. Thus salicylic acid heated with water in a sealed tube above 100° gives a solution which separates suddenly, on cooling to 91° , into two layers, each of which, according to Alexéef,* grows turbid independently as cooling goes on. Similar separations of liquids have been noticed by Hannay and Hogarth in the case of alcoholic solutions of calcic chloride and ferric chloride, under pressure. Moreover, the spontaneous separation, long suspected, of many saline solutions into layers of unlike density through the influence of gravity, has been confirmed by the studies of Bodländer and the more recent ones of Traube and Neuberg. The conversion of denser solutions into solid hydrous species is in many cases but a question of temperature. Liquidity is only an accident of solution. Not only is all solution chemical union, but "all chemical union is nothing else than

solution. The resulting species are, as it were, dissolved in each other, for solution is mutual." All precipitation and all crystallisation from solution thus involve chemical change, and all chemical species may theoretically exist in soluble states, from which they pass into polymeric mineral species, often insoluble.*

14. A given chemical species, whether elementary or complex in constitution, may in some cases pass through two or more higher *chemical forms*, by successive condensations, until at last it assumes a *mineral form* as a liquid or a solid species, which in the latter case may either be colloidal, or may take on a crystalline shape; the whole process, from the simplest chemical form, constituting an ascending series, in which the older and simpler forms are not lost but latent. It is to the converse of this process, or, in other words, to the depolymerisation by solution of solid mineral forms, that reference was had when, in 1853, the writer insisted upon "those chemical changes which commence only with the destruction of crystalline individuality," as quoted above in §4; or, in other words, to the breaking up of *mineral species* by solution into *chemical species*.

15. The mineral form itself is, however, in many cases subject to other changes, since the solid species may undergo alterations in density, in hardness, in fusibility and in crystalline shape without passing by a process of fusion or solution. Thus, for example, of the many allotropic phases of solid sulphur we may designate three as the plastic amorphous or colloidal, the clinorhombic and the orthorhombic. Of these, the first two pass spontaneously after a time into the denser and more stable orthorhombic state, an alteration which, as Spring has shown, is accelerated by pressure. A still more striking case is found in tin, the gray brittle form of which, with a density of 5.8 by gentle heat, concussion, or momentary pressure, passes into the white malleable species with the density 7.3, and may again by considerable reduction of temperature revert to the lighter brittle species. So the orthorhombic calcium carbonate, aragonite, is, at a low red heat, transformed into the lighter rhombohedral form, calcite. Ice, moreover, at 0° passes by pressure into liquid water, with a considerable increase of density (as in the case of tin); the transformations of the two species being readily repeated by slight variations of temperature or of pressure. It would be easy to multiply instances of such changes of mineral form.

16. In the case of insoluble non-volatile solids like tin and calcium carbonate we are precluded from the use alike of the vapour-density and the cryoscopic method as means of fixing the integral weight of the chemical species which by its polymerisation gives rise to the mineral species in question. We may add that even were the conditions such as to permit the application of either of these methods the presence of possible admixtures of different polymers might give rise to difficulties in their application, especially in cases where it is known that such polymers may have been simultaneously formed. Thus, for example, among the many polymers generated by the intrinsic condensation of acetylene, three, namely retene $(C_2H_2)_9$, cinnamene $(C_2H_2)_4$,—or rather its solid allotrope, metacinnamene—and benzene $(C_2H_2)_3$, are all solids at temperatures above 0° . An admixture of two or more of these might well have a fusing-point which would tend to confound it with some intermediate species. Again, among the higher olefines, $(CH_2)_n$, three of which have been mentioned above (§8), α -tridecylene ($n=18$), melts at 18° and has a density of 0.79; cerotene ($n=27$) melts at 58° and has a density of 0.86; while melene

* These views, set forth in 1853, and more fully in 1855, in "Thoughts on Solution and the Chemical Process," *Am. J. Sci.* (II.), xix., 100—103, and *Chemical Gazette* for 1855, p. 92, are reinforced in the "New Basis for Chemistry," pp. 98—99, and in "The Theory of Solution," *Brit. Assoc. Adv. Science*, Sec. B, 1888; *Chem. News*, lviii., 151. See also "Mineral Physiology, &c.," pp. 167—169. Similar views have since 1886 been put forward by Mendeléef.

($n=30$) melts at 62° and has a density of 0.89. Mixtures of any two of these would give rise to uncertainties like those which we have imagined in the case of the solid polymers of acetylene. In both these examples, it is true, separation of the intermingled hydrocarbons might be effected by differences in the solubility and the volatility of the polymeric species; but in other cases we have to deal with bodies alike non-volatile and insoluble, the problem becomes far more difficult. It is evident that, while in the case of gases and vapours the density varies directly as the integral weight of the chemical species, no such rule holds good in solids and liquids. This is well illustrated in the case of the three solid olefines just named, having, with small variations of density, integral weights for the chemical species which are to each other as 18 : 27 : 30, and also in that of the glucosic, diglucosic, and triglucosic sugars, having for the chemical species integral weights nearly as 1 : 2 : 3, yet with specific gravities for the solid or mineral species which are almost identical.

17. Among native mineral species there are not wanting instances of such mixtures, a good example being seen in the disulphide of iron, which constitutes alike the orthorhombic species marcasite, and the isometric species pyrite. Multiplied observations of specimens of the latter species by various skilled naturalists show that its specific gravity may vary from 4.80 to 5.00 and even 5.15 and 5.20 for well-defined pyritohedral crystals. On the other hand, marcasite itself may vary in specific gravity from 4.75 to about 5.00 (4.987), with a hardness on the scale of Mohs of 6.0–6.5; while the denser isometric species attains 6.5–7.0. The latter strikes fire strongly with steel, giving a faint sulphurous odour; marcasite, on the contrary, feebly, giving a strong odour. Differences in colour and texture also distinguish the denser from the lighter sulphide. A. A. Julien, who has lately examined this question with great care, concludes that we have in these minerals of intermediate density an intermingling of two disulphides of unlike degrees of condensation. Each of these species would thus be dimorphous, and might include admixtures of the other.* It is difficult to conceive any other explanation of these facts, which are precisely what we should expect in the case of admixtures of polymeric bodies like the hydrocarbons noted above. It will be found that an admixture of three parts of a disulphide of iron, sp. gr. 5.18, and two parts of one of sp. gr. 4.75, would give a mean sp. gr. of 5.00, which is that assigned by many observers to pyrite, and very near the maximum specific gravity of marcasite.

Similar differences in density are met with among the orthorhombic and isometric arsenides of cobalt, nickel, and iron, represented by the general formula MA_2 , as shown in safflorite and smaltite, verified by the recent studies of MacCay. Another example of the kind, uncomplicated by the question of dimorphism, is seen in sodium chloride. Several careful observers concur in giving for specimens of this substance at ordinary temperatures a specific gravity of about 2.25 (2.20, 2.23, 2.26); and others, apparently equally worthy of confidence, have found about 2.00 (2.01, 2.03, 2.06, 2.08), while the greater number of observations range from 2.14 to 2.20. These wide variations in density in such a familiar species are the more remarkable for the reason that the chlorides of potassium and ammonium present no such notable variations. A similar condition of things is apparent in crystals of zircon, and many other cases might be cited showing that we have, as in the case of the iron disulphides, variable admixtures of two mineral species with the same centesimal composition but of unlike condensation.

18. It will now be apparent that we have to deal with processes of condensation belonging alike to chemical species and to mineral species. Thus, for example, with acetylene, pentene, and their polymers, we have in each case chemical species having a common centesimal com-

position with widely different coefficients of chemical condensation, as is apparent when we compare their vapour-densities; which, moreover, present no simple or apparent relations to their specific gravities in the liquid or solid state. We may recall in this connection the already cited case of formaldehyd, of which the equivalent weight is fixed by its vapour-density as well as by Raoult's method, with those of xylose, glucose, and the related sugars and amyloid bodies; species for which the chemical condensation presents a very wide range. In these cases we are enabled by vapour-density, by the cryoscopic method, or else by direct chemical analysis, to determine the minimum value of the chemical integer, and in this latter way we are led to assign in many cases very elevated numbers, as seen in such compounds as the cobaltamine salts and the polytungstates, the simplest admissible formulæ of which give integral weights of thousands or tens of thousands.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 4th, 1890.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Charles Henry Corbett, Barnard Castle; Hendrick Thomas Donovan, Crumpton Street, Bridgetown, Barbadoes; Henry Charles Jenkins, Lorne Villa, Iveson Road, Hampstead; William Morley Martin, Cardrew, Redruth; Arnold Whitaker Oxford, 8, Henrietta Street, Cavendish Square, W.; Frederick William De Velling, High Street, Heckmondwike, Yorkshire; Herbert D. Shaw, Castle Mount, Sandal, nr. Wakefield; R. Stockdale, The Grammar School, Leeds; Kenelm Edward Symes, Magdalen House, Bridport, Dorset.

The following were elected Fellows of the Society:—Messrs. Gustavus Anthony Abrines; John Thomas Brierley; William J. Butcher; William Waters Butler; Frank Brownswold; M. Kelway Bamber; Ernest Bents; W. E. B. Blenkinsop; Thomas Arthur Cheetham; Arthur William Crosskey; Arthur William Cooke; William L. Dudley; Thomas S. Goodwin; Alfred Henry Green; William Mahowe Heller; John Richard Jackson; Joseph Lunt; Harry C. Myers; William Mackeay; Thomas Smith Murray; William Reginald Ormandy; James Alexander Pond; Thomas Platts; G. H. Robertson; Ernest Henry Sainter; Thomas Steel; John Joseph Sudborough; Charles Thomas Sprayne; Francis Henry Tate; George Henry Wadsworth; Sidney Wood; George Young.

The following papers were read:—

95. "The Action of Heat on Ethylic β -Amidocrotonate." Part I. By J. NORMAN COLLIE, University College, London.

Some years ago, whilst working with ethylic β -amidocrotonate, the author noticed that during its purification by distillation under reduced pressure a crystalline compound of the formula—



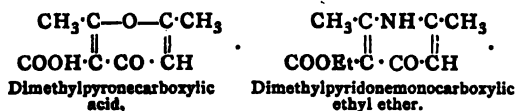
was always produced in small quantities, and remained behind in the fractionating flask. This condensation product was found to be the ethylic salt of an acid $C_8H_7NO_3$, which from its properties was considered to be the monocarboxylic acid of a hydroxylutidine. Owing to the small quantities obtained, the investigation was carried no further. Since then, having had to work with large amounts of ethylic β -amidocrotonate, a further supply of the condensation compound has been obtained, and a

* A. A. Julien, *N. Y. Acad. Sci.*, 1886, 1887, vol. iii., No. 12, iv., Nos. 3, 5, 6, 7.

more exact study of its derivatives has been possible. The author now finds that the acid is *not* a hydroxyl derivative of lutidine, but *lutidomonicarboxylic acid*, for on heating it yields carbon dioxide and lutidone or *αα*-dimethylpyridone. This partial decomposition by heat of ethylic *β*-amidocrotonate is therefore very similar to that which ethylic acetoacetate undergoes in its conversion into dehydracetic acid during distillation:—



Feist in his interesting paper on dehydracetic acid (*Annalen*, cclvii., 253) has shown that it is easily converted into dimethylpyronecarboxylic acid, the oxygen analogue of dimethylpyridonecarboxylic acid:—



Ethylic lutidonemonocarboxylate does not decompose when boiled with caustic soda, but is merely hydrolysed and converted into the sodium salt of the acid; with phenylhydrazine and hydroxylamine it also does not form any compounds, and thus differs from dehydracetic acid. With bromine it forms a monobrominated derivative, $C_{12}H_{12}NO_3Br$, and with pentachloride of phosphorus the compound $C_{10}H_{12}NO_2Cl$. The acid obtained from the sodium salt melts at $247^\circ C.$, decomposing at the same time into carbon dioxide and a compound which agrees in every respect with the *αα*-dimethylpyridone, C_7H_9NO , obtained by Haitinger from dehydracetic acid, and also by Conrad and Geutzeit by heating lutidonedicarboxylic acid. This lutidone when heated with zinc-dust yields, according to Haitinger, *αα*-dimethylpyridine boiling at $148-151^\circ C.$, whilst the *αα*-dimethylpyridine obtained from other sources boils at $142-143^\circ C.$ Conrad and Geutzeit also obtained a lutidine from this lutidone, but do not give its boiling point. The author has been able to obtain a lutidine by four different methods:—

- (1). By distillation of the potassium salt of lutidonecarboxylic acid with excess of solid caustic potash.
- (2). By the prolonged action of nascent hydrogen (from tin and hydrochloric acid) on the chlorolutidine obtained by treating the lutidone with pentachloride of phosphorus.
- (3). By heating the chlorolutidine with zinc-dust in an atmosphere of hydrogen.
- (4). By heating the chlorolutidine obtained from dehydracetic acid by Haitinger's method with zinc-dust.

All these four methods gave a lutidine boiling at $144-145^\circ C.$, and yielding a platinum salt melting at $210-212^\circ C.$, the melting-point found by Epstein and Ladenburg for the chloroplatinate of *αα*-dimethylpyridine. The author has also been able to compare this lutidine with a lutidine boiling at $143-144^\circ$ obtained by Professor Ramsay from bone oil, and is led to regard it as identical therewith. By oxidation of the lutidine from ethylic *β*-amidocrotonate with potassium permanganate, a pyridinedicarboxylic acid was obtained melting at $235^\circ C.$ (corr.), which, on heating, gave pyridine, showing that it was dipicolinic or *αα*-pyridinedicarboxylic acid.

96. "The Action of Heat on Nitrosyl Chloride." By J. J. SUBBOROUGH, B.Sc. (Lond.), and G. H. MILLER.

An account is given of a series of determinations of the vapour-density of nitrosyl chloride, $NOCl$, at various temperatures. At temperatures from 15° to 693° , the values obtained so nearly coincide with the theoretical value 32.67 , that it is to be supposed that no dissociation takes place below about 700° . At higher temperatures, the compound is no longer stable, as the following numbers show:—(See Table, next column).

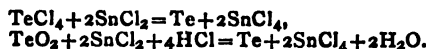
The results show that in comparison with nitrogen dioxide, NO_2 , which is completely decomposed below 620° , nitrosyl chloride is a highly stable compound.

Temperature.	Vapour-density.
784°	31.77
796	31.36
815	31.00
928	29.00
968	27.30
985	27.00

Nitrosyl chloride in its reactions with water behaves as the chloride of nitrous acid, and inasmuch as nitrous acid not only forms nitroso-compounds, but also hydroximes by interaction with the CH_2 group, nitrous acid would appear to have the formula $O:N\cdot OH$, and the chloride the formula $O:N\cdot Cl$. As nitric oxide and nitrosyl chloride show no tendency to polymerise, the union which takes place between NO_2 and NO at temperatures below 140° is probably established between oxygen atoms, and as only like molecules of NO_2 are concerned in the formation of nitrogen peroxide, it is unlikely that the latter as an unsymmetrical formula: the formula $O:N\cdot O\cdot N\cdot O$ would appear to satisfy the requirements of the case; this leads to the formula $O:N\cdot O$ for the dioxide, and it may be that the instability of the dioxide is due to the unsaturated condition of the oxygen.

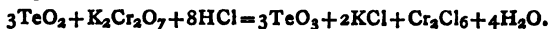
97. "The Volumetric Estimation of Tellurium." By Dr. B. BRAUNER.

Hitherto only gravimetric methods have been adopted in estimating tellurium, and as they involve the use of weighed filters, the determination is subject to considerable error, besides occupying much time. The author describes two volumetric processes. The first is based on the reduction of solutions of tellurium dioxide by stannous chloride:—



The tellurium compound, together with muriatic acid, is digested with excess of stannous chloride, and the excess subsequently determined by iodine and thiosulphate.

The second method consists in adding an excess of potassium dichromate solution to the solution of tellurium dioxide in muriatic acid, the excess of dichromate being subsequently determined by means of ammonium ferrous sulphate:—



Results are quoted showing that the first method gives satisfactory results; but the second does not appear to be one of practical value.

NOTICES OF BOOKS.

Outlines of General Chemistry. By W. OSTWALD, Professor of Chemistry in the University of Leipzig. Translated, with the Author's Sanction, by JAMES WALKER, D.Sc., Ph.D. London: Macmillan and Co.

THE author of this profoundly able and interesting work has found his task rendered more difficult because "the course of study still pursued by the average chemist has laid upon him the necessity of the employment of higher mathematics." Again, he writes: "That the reader who has only an acquaintance with elementary mathematics may be brought to see the necessity of acquiring at least the rudiments of the higher analysis." If such acquirement is a "necessity," chemistry will lose many followers who are capable of doing useful work. Higher mathematics will always be a speciality of one type of minds.

The complaint of the author and the translator that the researches of Van't Hoff on the theory of solution and those of Arrhenius on electrolytic dissociation have not met with due attention in this country is well founded, and we

share the hope that the appearance of this work in an English version may cause this neglect to disappear.

Prof. Ostwald discusses in his first part the chemical laws of mass, and in the second those of energy. The former part treats, in succession, of mass, of the properties of gases, of liquids, of solutions, of solids, and of chemical systematics.

The elements he accepts as undecomposed, but not necessarily undecomposable. But he holds that if "composite, they are all composite to the same degree,"—a conclusion which is perhaps still open to doubt.

Concerning Prout's law, the author leaves unanswered the question why the atomic weights of so many elements approximate so closely to multiples of hydrogen. A similar approximation, without identity being reached, appears in the triads of Döbereiner and Lenz.

In the discussion of the periodic law, the first enunciation of the idea is ascribed to Newlands, with the remark that he "did not succeed in fully carrying it out," and that it failed to find ready recognition, as presented in a "somewhat inadequate form." Prof. Ostwald, whilst recognising that "almost every well-defined and comparable property appears as a periodic function of the atomic weight," considers that the periodic system of the elements is by no means perfect. He reminds us that "elements are frequently parted in the tables which an unprejudiced observer would consider analogous in their compounds (e.g., copper and mercury), whilst others are placed together which appear altogether dissimilar, as sodium, copper, silver, and gold." Further, Mendeleeff has called the elements with the lowest atomic weights the "typical elements." This, remarks the author, "is a name signifying just the opposite of what is really meant, for these elements are by no means typical of the groups whose first members they constitute." These criticisms cannot be pronounced other than just and weighty.

In the determination of the atomic weights, the author prefers to return to the unit of Berzelius and put, arbitrarily, $O=16$.

On the subject of structural formulæ, Prof. Ostwald expresses himself very judiciously. He considers that they stand in much the same relation to the substances they represent as do formulæ of analytical geometry to the corresponding curves and surfaces, though they do not approach the latter in certainty and completeness of expression.

The tri-dimensional formulation of atomic space-relations, as propounded first by Van't Hoff and afterwards by Wislicenus, is explained by examples. Various phenomena, hitherto incomprehensible, can thus be explained. It is to be hoped that this idea will meet with more attention than it has hitherto received, both among teachers and students.

The second part of the work, devoted to the chemical laws of energy, discusses, in succession, thermo-chemistry, photo-chemistry, electro-chemistry, and chemical dynamics.

Unlike many German books, these "Outlines" are furnished with an excellent index of subjects, and, in addition, with one of the names of authors referred to. Advanced students will find in the work before us not merely a clear oversight of the philosophy of chemistry as at present understood, but a guide to subjects for future research. It would be at once interesting and instructive to compare Ostwald's Outlines with Daubeny's Atomic Theory, or any other theoretical work of the first half of the century.

An Impurity in White Wine Vinegars.—A. Held.—In a sample sold as white wine vinegar, the author finds a considerable quantity of amylic alcohol. The vinegar in question contained no potassium bitartrate, and was merely the product of the acetic fermentation of an alcohol containing much amylic alcohol.—*Journal de Pharm. et de Chimie.*

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—I am greatly surprised at the letter of Messrs. Bloxam and Blount in your issue of the 12th inst., and I may say that if the Council of the Society adopt their suggestion of advertising, twenty-five friends as well as myself will at once resign our memberships. Let it be understood that we are non-trading members.

Just fancy a distinguished and learned society like the Chemical Society of London advertising itself as suggested by Messrs. Bloxam and Blount!—I am, &c.,

A CONTRIBUTOR TO THE
Journal of the Chemical Society.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—I did not sign the circular from Messrs. Lloyd and Teed, whose object was, no doubt, the supposed welfare of the Society. The means proposed seem inquisitorial, and might suggest that the letter C in F.C.S. should stand for "Censorial." I do not see the need for so great a change. We are not called upon to apportion the exact weight which the public should attach to the letters F.C.S. Why not let well alone? If any are using the Fellowship for trade purposes, would not a remonstrance be best, drawing the delinquent's attention to the declaration against it which he signed on admission?—I am, &c.,

F.C.S.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—There appears to be a necessity for a re-statement of the main facts upon which the present situation must be resolved. These are:—

(1.) The Society imposes upon candidates for the Fellowship a certain standard of qualification—whether social or scientific. Unless, therefore, the present form of election be abandoned, the Fellowship must continue so far to constitute a "qualification;" and for any Fellow to maintain the opposite is an obvious stultification.

(2.) The constitution of the Society is democratic in principle, though the actual management of its affairs is by tacit consent autocratic, as indeed it should be.

In other words, it is in the power of the majority of the Fellows to determine any course of action within the limits of the constitution of the Society, by electing an executive representative of its views, and pledged to give effect to its will.

I venture to think that some of your correspondents on this subject are disposed to ignore these prominent factors of the situation.—I am, &c.,

A FELLOW.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—Messrs. Bloxam and Blount's difficulties seem to me not difficult to answer.

First, the Society has never encouraged the alleged view as to the qualifying value of the Fellowship, which, if it exists, has been conferred on it by the public. The Society is not responsible for this, and has done its best

to discourage it by freely admitting all interested in the science, as its charter requires.

Second, the charter is absolutely silent as to a qualification, and expressly withholds the power to make any bye-law "in opposition to the general scope, true intent, and meaning of this our charter." It is manifest that nothing short of an amendment of the charter will get over this.

Third, many of us think that the present system is sufficient, and that the exaggerated view, if it exists, will gradually fade as the true function of the Institute of Chemistry comes into greater prominence. But admitting all the alleged evils, surely wild blackballing is not the way to mend them; for, as Messrs. Bloxam and Blount themselves point out, either all or no candidates must be admitted; no doubt reading "all" as equivalent to all persons of good character, and "no" as none without an examination; for they surely do not intend to assert that a chance meeting of the Chemical Society could ever become an efficient qualifying body.

Mr. Livingstone has misunderstood my letter in your issue of December 5th, as the grounds of my assumptions were there given and require no explanation.—I am, &c.,

R. J. FRISWELL.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxl., No. 22, December 1, 1890.

Compressibility of Mixtures of Air and of Carbon Dioxide.—M. Ulysse Lala.—The compressibility of mixtures of dry air and of carbon dioxide when the quantity of the latter does not exceed 22 per cent is comprised between those of air and carbon dioxide. The compressibility of higher mixtures is greater than that of carbon dioxide.

A New Process for Distinguishing Arsenical and Antimonial Spots.—G. Denigès.—H. Rose pointed out long ago that arsenic acid behaves like phosphoric acid with a nitric solution of ammonium molybdate. This reaction has been utilised for the detection or determination of arsenic acid or arseniates; but it does not seem to have been applied in toxicology for distinguishing arsenical spots from those of antimony. The production of crystals of ammonium arsenio-molybdate is very easy, and this substance is distinguished by its fine yellow colour, its insolubility in nitric acid, and especially by its microscopic appearance in the form of stars with triangular branches, generally six in number, and arranged in rectangular planes according to the axes of a cube. These crystals appear very distinctly under the polarising microscope when the analyser and the polariser are turned to extinction. It must be said that ammonium phosphomolybdate presents quite identical appearance and properties; but as no trace of phosphoric products can exist in the arsenical or antimonial spots furnished by the apparatus of Marsh, it is legitimate to infer the presence of arsenic whenever we obtain yellow crystals presenting the characters described above. The suspected spots, collected in a small porcelain capsule, are mixed with a few drops of pure nitric acid; they dissolve instantly, whether they consist of antimony or arsenic. Heat is applied for a few moments to complete the oxidation, and there are added four or five drops of ammonium molybdate in a nitric solution. There is soon formed, even if there are only traces of arsenic (from 1-50 to 1-100 of a milligramme), a yellow precipitate which on examination

with the microscope shows the forms above described. Antimony gives nothing analogous. The reaction just pointed out seems the most sensitive and the most characteristic. It is easy to produce and is applicable to the determination of very small quantities of arsenic, as the author purposes to explain in a further communication. The molybdic reagent employed is prepared as follows:—Dissolve at a gentle heat 10 grms. commercial ammonium molybdate (hexammonium heptamolybdate), and 25 grms. ammonium nitrate in 100 c.c. water. Let cool, and add gradually, while stirring, 100 c.c. pure nitric acid of specific gravity 1.20. Heat on the water-bath for ten minutes, let cool, and leave it for 48 hours. At the end of this time filter through paper washed with dilute nitric acid and keep in stoppered bottles.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iv., Nos. 4 and 5.

On the Formation and the Combustion Heats of Various Nitrogenous Principles Derived from Albumenoid Matters.—MM. Berthelot and André.—The total combustion heat of the nitrogenous principles, urea and leucine excepted, exceeds that which would be calculated on the hypothesis that hydrogen separated in the state of water does not evolve any heat, and that the carbon generates as much as if it were free.

Formation-Heat of Certain Amides.—MM. Berthelot and Fogh.—The formation of anilides from the solid acid and the gaseous base evolves more heat than that of the corresponding amides; a circumstance correlated to a greater stability against the decomposing action of water.

Combustion-Heat of the Chief Nitrogenous Principles Contained in Living Beings and its Part in the Production of Animal Heat.—MM. Berthelot and André.—The authors give their results in the form of a table.

The Reduction of Alkaline Sulphates by Hydrogen and by Carbon.—M. Berthelot.—Not adapted for useful abridgment.

Thermic Researches on the Allotropic Conditions of Arsenic.—MM. Berthelot and Engel.—The two varieties of arsenic evolve almost identical quantities of heat whilst forming one and the same compound. Their relations are similar to those existing between graphite and diamond.

On the Formation-Heat and the Reactions of Hydroxylamine or Oxyammonia.—MM. Berthelot and André.—A thermo-chemical study of hydroxylamine nitrate. The conversion of ammonia into hydroxylamine, whether free or dissolved, is not an oxidation.

New Researches on the Relative Stability of Salts, both Isolated and in Presence of Water. Salts of Aniline.—M. Berthelot.—The formation-heat of salts referred to the solid state may be taken as the measure of their relative stability.

On the Isomeric Inosites and on their Transformation-Heat.—M. Berthelot.—The two symmetric inosites in a state of solution do not manifest any sign of combination any more than do the two symmetric tartaric acids. But the combination takes place as soon as they are separated from their solutions.

Researches on Certain Saccharine Principles.—MM. Berthelot and Matignon.—The true inactive nosite appears to contain a reserve of energy superior to that of the other isomers which it is apt to produce; whilst the neutral inosite, the molecule of which is double, corresponds to the greatest loss of energy.

The Oxidation of the Sulphur of Organic Compounds.—MM. Berthelot, André, and Matignon.—The authors burn the sulphuretted organic compound in the "calorimetric bomb" in an atmosphere of oxygen com-

pressed at 25 atmospheres and in presence of 10 centimetres of water.

Combustion-Heat of Certain Sulphur Compounds.—MM. Berthelot and Matignon.—The compounds in question are thiophene, taurine, and carbon disulphide.

Analysis of an Argentocupric Mineral.—Prof. E. Jacquemin.—This mineral, from Bussang, in the Vosges, and known locally as "green stones," contains, according to the samples examined, 210–225 grms. silver per ton—a quantity which admits of working, especially as the copper alone, which varies from 35 to 45 kilos. per ton, is remunerative.

Preparation of Certain Ethers by Fermentation.—Georges Jacquemin.—From a fermentation effected in the absence of air, the author obtained a large proportion of butyric ether and of ethylic ether mixed with higher alcohols.

The Preparation and Properties of Aricine.—H. Moissan and E. Landrin.—The bark operated upon contained neither quinine nor cinchonine. Aricine has a composition expressed by the formula $C_{46}H_{26}N_2O_8$. It forms fine transparent crystals, which, on prolonged exposure to the sun, turn slightly yellow. It is insoluble in water, soluble in alcohol at common temperatures, but more soluble at a boiling-heat. At 15° ether dissolves 30 grms. per litre. It melts at 188–189°.

New Preparation of Phosphorus Oxyfluoride.—Henri Moissan.—The authors cause phosphorus oxychloride to act upon anhydrous zinc fluoride (not ignited) in a metal vessel. The product obtained is a gaseous body absorbable in water, which decomposes it, and fuming in the air.

On the Critical Temperature.—M. Philippe and A. Guye.—From the tables given the authors conclude that the critical temperature is approximately equal to twice the boiling temperature *in vacuo* (20 m.m.). It is approximately equal to 4.55 times the temperature of ebullition under the atmospheric pressure.

On Fluorene Hydrides.—P. A. Guye.—The author has obtained a decahydride and an octohydride of fluorene and an octohydride of phenanthrene.

Vol. iv., Nos. 6 and 7.

Action of Mineral Acids upon the Lactic and the Butyric Ferments.—Dr. J. Effront.—The action of the mineral acids upon the lactic ferment is the same as that of the lactic acid formed in the course of fermentation; they enfeeble or entirely kill the ferments. Hydrofluoric acid acts much more energetically than the hydrochloric and the sulphuric. In the butyric fermentation the results are analogous.

Action of Isopropyl Iodide upon Aqueous Ammonia in Equi-molecular Proportion at the Ambient Temperature.—H. Malbot.—Under such conditions isopropyl iodide is converted almost entirely into mono-isopropylamine hydriodate.

The Filtration of Wort of Green Malt and Maize, through a Chamberland Filter.—The Chamberland filter holds back dextrine, albumen, and mineral matters, to a considerable proportion.

The Composition of Kaolinic Porcelains.—Georges Vogt.—This memoir will be inserted at some length.

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ST. PAUL'S SCHOOL.—An Examination for filling up about Five Vacancies on the Foundation will be held on the 14th January next.—For information apply to the Bursar, St. Paul's School, West Kensington.

THE CHEMICAL NEWS.

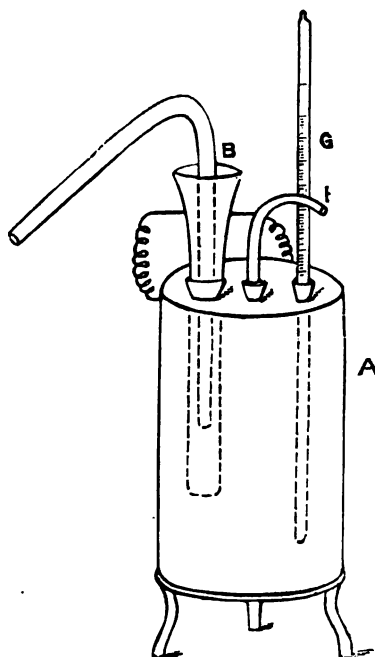
VOL. LXII. No. 1622.

A SIMPLE ELECTRICAL APPARATUS FOR DETERMINING THE FLASHING POINT OF MINERAL OILS.

By H. N. WARREN, Research Analyst.

THIS simple yet effective apparatus may be readily constructed from an ordinary tin canister as shown by the accompanying diagram. A represents either a copper or tinned iron cylinder, supported on tripod legs, and capable of holding about a litre of water. B is a wide-mouthed test-tube into which are fused two platinum wires connected respectively to a good induction coil capable of producing about a half inch spark. In using the apparatus the steam-pipe *r*, which is maintained in its place by inserting it through a perforated cork, is first removed and water introduced into the boiler, the tubular being replaced.

Into the tube B is placed about an ounce of the oil under question, and a light applied to the canister; the contact breaker of the induction coil should be now so regulated as to allow of a spark being passed across the tube B when desired, by merely touching the hammer.



When the apparatus has reached a temperature of about 100° F., a spark may be conveniently applied. If the effect of the explosion is somewhat violent, the light should be removed and a spark passed every few seconds until it ceases to afford any further detonation. When this point is reached it is regarded as the flashing point of the oil, and is at once indicated by the reading of the thermometer, G, which should remain inserted in the water contained in the apparatus during the testing operation. For accurate results care must be taken that any explosive residue that may remain in the tube after the passing of a former spark be removed by injecting a small quantity

of air from the mouth by means of the syphon, &c; otherwise on the admittance of a further spark a partially exhausted atmosphere may be unintentionally re-examined at a lower temperature. With due precautions the apparatus affords accurate results, and a large number of samples may be tested at a brief notice.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

THE ANALYSIS OF WATER TO DETERMINE SCALE-FORMING INGREDIENTS.*

By Prof. THOMAS B. STILLMAN.

(Concluded from p. 300).

It is necessary now to convert these values, grms. per litre, into grains per gallon, in doing which the following table is used:—

Table for Converting M. grms. per Litre into Grains per U.S. Gallon of 231 Cubic Inches.

M. grms. per litre.	Grains per gallon.	M. grms. per litre.	Grains per gallon.
1	=0'0583	51	=2'9742
2	0'1166	52	3'0325
3	0'1749	53	3'0908
4	0'2332	54	3'1491
5	0'2915	55	3'2074
6	0'3499	56	3'2658
7	0'4082	57	3'3241
8	0'4665	58	3'3824
9	0'5248	59	3'4407
10	0'5831	60	3'4990
11	0'6414	61	3'5573
12	0'6998	62	3'6157
13	0'7581	63	3'6740
14	0'8165	64	3'7323
15	0'8747	65	3'7906
16	0'9330	66	3'8489
17	0'9914	67	3'9073
18	1'0497	68	3'9656
19	1'1080	69	4'0239
20	1'1663	70	4'0822
21	1'2246	71	4'1405
22	1'2829	72	4'1988
23	1'3413	73	4'2572
24	1'3996	74	4'3155
25	1'4579	75	4'3738
26	1'5162	76	4'4321
27	1'5745	77	4'4904
28	1'6329	78	4'5488
29	1'6912	79	4'6071
30	1'7495	80	4'6654
31	1'8078	81	4'7237
32	1'8661	82	4'7820
33	1'9244	83	4'8403
34	1'9828	84	4'8987
35	2'0411	85	4'9570
36	2'0994	86	5'0153
37	2'1577	87	5'0736
38	2'2160	88	5'1319
39	2'2745	89	5'1903
40	2'3327	90	5'2486
41	2'3910	91	5'3069
42	2'4493	92	5'3652
43	2'5076	93	5'4235
44	2'5659	94	5'4818
45	2'6243	95	5'5402
46	2'6826	96	5'5985
47	2'7409	97	5'6568
48	2'7992	98	5'7151
49	2'8575	99	5'7734
50	2'9159	100	5'8318

* The Stevens Indicator, vol. vii., No. 4, Oct., 1890.

— Jan. Analyst Chem

The amounts obtained being:—

	Grains per gallon.
Silica	0'4771
SO ₃	1'2012
Cl	0'3206
K ₂ O	0'0291
Na ₂ O	0'3615
MgO	0'4490
CaO	1'1313
Fe ₂ O ₃ Al ₂ O ₃	0'2973
Organic	1'1254
Carbonic acid	0'7989
	6'1914
Oxygen in excess of Cl	0'0932
	6'0982

Having determined the component parts of the water residue in grains per gallon, it becomes necessary to unite these in chemical union, as near as possible, as they exist in the water.

The general rule may be stated as follows:—The chlorine is combined with the sodium, if still in excess, then with the potassium, magnesium, and finally calcium. The sulphuric acid to the alkalies, provided there is not enough chlorine to saturate them, then to the calcium, and finally to the magnesium.

The carbonic acid is united with the calcium and magnesium after the other combinations are made. There are exceptions to this rule, mineral waters and many artesian well waters forming notable examples.

Carrying out the above, the following is obtained:—

	Grms. per litre.	Grains per gallon.
NaCl	0'0091	0'5306
Na ₂ SO ₄	0'0033	0'1923
K ₂ SO ₄	0'0009	0'0524
CaSO ₄	0'0311	1'8136
CaCO ₃	0'0118	0'6880
MgCO ₃	0'0162	0'9446
Fe ₂ O ₃ Al ₂ O ₃	0'0051	0'2973
SiO ₂	0'0082	0'4771
Organic, &c.	0'0193	1'1254
Total	0'1050	6'1213

This analysis shows that the principal scale-forming ingredient is calcium sulphate, being more than equal to the carbonates of calcium and magnesium.

The following analysis is of a water containing sulphuric acid, but the alkalies being present in sufficient amount to combine with all of it, as well as the chlorine, no sulphate of lime is present.

	Grms. per litre.	Grains per gallon.
SiO ₂	0'0038	0'2215
So ₃	0'0110	0'6414
Cl	0'0062	0'3615
K ₂ O	0'0033	0'1923
Na ₂ O	0'0185	1'0788
MgO	0'0165	0'9388
CaO	0'0466	2'7175
Al ₂ O ₃ Fe ₂ O ₃	0'0020	0'1166
Organic	0'0246	1'4345
Carbonic acid	0'0530	3'0908
	0'1851	10'7937
Oxygen in excess of Cl	0'0021	0'1224
Total	0'1830	10'6713

Combined as follows:—

NaCl	0'0154	0'8900
Na ₂ SO ₄	0'0141	0'8223
K ₂ SO ₄	0'0061	0'5557
CaCO ₃	0'0833	4'8577
MgCO ₃	0'0338	1'9710
Al ₂ O ₃ Fe ₂ O ₃	0'0020	0'1166
SiO ₂	0'0038	0'2215
Organic	0'0246	1'4345
Total	0'1831	10'6773

Where all the chlorine is not in combination with the sodium and potassium, chloride of magnesium is usually present.

This latter compound, while not scale-forming, is considered as an active corrosive agent—upon the supposition that at the temperature of 100° C., and higher, it is decomposed, and hydrochloric acid formed and liberated—consult *Journal Society of Chemical Industry*, vol. ix., p. 472; also, "Treatise on Steam Boilers," by Wilson, p. 168.

The report, given below, is of a water from a driven well in Florida. Complaint having been made that not only was the scale excessive in amount, but that corrosive action was also very marked, an analysis was made, reference to which readily explains the difficulty encountered in the boilers.

	Grms. per litre.	Grains per gallon.
NaCl	0'323	18'87
KCl	0'067	3'91
MgCl ₂	0'104	6'06
CaSO ₄	0'197	11'52
CaCO ₃	0'293	17'10
MgCO ₃	0'144	8'40
SiO ₂	0'011	0'62
Al ₂ O ₃ Fe ₂ O ₃	0'007	0'46
Organic	0'138	8'02
Total	1'284	74'86

In all of the above analyses the constituents have been stated in grains per gallon, rather than in parts per 100,000, the former being in general use by the mechanical profession as the proper method by which to express the weights of the component parts of a water.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1890.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, *Metropolis Water Act*, 1871.

London, December 6th, 1890.

SIR,—We submit herewith the results of our analyses of the 167 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from November 1st to November 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 167 samples examined, the whole (excepting two samples which were recorded as "very slightly turbid") were found to be clear, bright, and well filtered.

The seasonal variation in the composition of the water supplied to the Metropolis, for the most part too slight to constitute a variation in character, has, with the coming on of winter, to be looked for and taken note of. As regards the November supply, however, the less favourable meteorological conditions prevailing during the month including occasional periods of frost, were not found to have any significant effect on the analytical results obtained. Both absolutely, and still more in relation to the season, these results were entirely satisfactory. Thus, in the case of the Thames-derived water, the mean proportion of organic carbon was found to be 0.142 part in 100,000 parts of the water, with a maximum of 0.158 in any single sample examined, as against a mean of 0.136 part, and a maximum of 0.160 part met with in the previous month's supply. Similarly, the mean amount of oxygen consumed in the oxidation of the organic matter present in a gallon of the water was found to be 0.046 grain, against 0.040 grain (printed by mistake as 0.40 grain in the previous month's report), in the previous month's supply. Moreover, the degree of freedom from colour-tint continued to be good, the ratio of brown to blue-tint of the water being as 13.1 : 20, as against a ratio of 10.4 : 20 recorded in October, and a ratio of 14.1 : 20 recorded in September last.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

WILLIAM ODLING.

C. MEYMOTT TIDY.

ALLOYS OF SODIUM AND LEAD.*

By W. H. GREENE and W. H. WAHL.

RECENTLY, in the course of certain investigations in which we had occasion to make use of alloys of lead and sodium, we found that the properties of such alloys did not correspond with what we had anticipated from previous publications on the subject, and we were led to an examination of the properties of lead-sodium alloys of definite composition. These alloys may easily be made by direct combination, and the products are then sensibly constant in composition, which is not the case when they are prepared by reducing lead oxide by carbon in presence of soda, or by heating litharge with sodium tartrate, as described by Vauquelin and Serullas.

The required quantity of sodium was added to lead melted in a covered crucible, and the alloy was roughly analysed by determining lead only. Our alloys contained from 3 to 31 per cent sodium. They are all brittle and crystalline; all decompose water, that containing the least sodium producing a hardly perceptible evolution of gas, while that containing 31 per cent reacts with violence. The brittleness and oxidability increase with the percentage of sodium. The richest alloy is greenish in colour and instantly blackens on exposure to air.

We made special examinations of the alloys, corresponding in composition to Na_2Pb_2 , Na_2Pb , and Na_4Pb ; the first of these contained 10 per cent sodium, the second 19.5 per cent, rather more than would be indicated by the formula, while the last contained 31.7 per cent. The densities were determined in aniline and found to be

considerably higher than would be the densities of mixtures of the same composition. Thus the 10 per cent alloy has a density of 6.91, the 19.5 per cent a density of 4.61, and the 31.7 per cent alloy a density of 3.81. The densities of corresponding mixtures would be 5.6, 3.7, and 2.7 respectively.

The theoretical and calculated percentages of Na in alloys of above assumed composition compare as follows:—

	Na_2Pb_2 .	Na_2Pb .	Na_4Pb .
P.c. Na by theory ..	10	18.18	30.8
„ found ..	10	19.5	31.7

SIMULTANEOUS DETECTION OF THE HALOID SALTS, AND IN PARTICULAR OF CHLORIDES IN PRESENCE OF BROMIDES.

By G. DENIGÈS.

A VERY easy and characteristic means of detecting chlorine or bromine in a gaseous atmosphere is to plunge into it a glass rod, previously steeped in an alkaline lye (which, in contact with the halogens, is converted into a hypochlorite or hypobromite), and to dip the moist end of this rod in a saturated solution of aniline in water, which is coloured violet or violet-red by the hypochlorites and orange-yellow by the hypobromites.

If we have a mixture of haloid salts we need, therefore, merely to set the halogens at liberty in order to detect them by the aniline method. For this purpose we generally employ sulphuric acid and an oxidising substance, most commonly manganese peroxide; among the other oxidising agents the chromates liberate only iodine and bromine without sensibly affecting the chlorides. Permanganate quickly sets all the halogens at liberty.

On the basis of these facts, the author has devised the following method for the easy and expeditious detection of chlorides in presence of bromides, and in a more general manner for the simultaneous recognition of all the haloid salts.

For this purpose a c.c. of the liquid to be examined is put into a test-tube, and there are added from 20 to 30 drops of concentrated sulphuric acid. If a gas escapes (carbonic, sulphurous, &c.) the mixture is boiled to expel it, and there are added 20—30 drops of a solution (saturated in the cold) of yellow potassium chromate (about 50 grms. of the salt to 100 c.c. of water); into the first half of the tube there is plunged a slip of starch paper moistened with water, which, if it turns blue indicates the presence of iodine, or otherwise its absence.

In the latter case we add a few drops more of sulphuric acid, and plunge into the axis of the tube (without touching the sides) a glass rod, the rounded extremity of which has been moistened with soap-boilers' lye (!) After a few seconds it is withdrawn, and the moistened end is brought in contact, in a glass, with a c.c. of water saturated with aniline, and stirred. If there is produced an orange precipitate the liquid contains a bromide. If there is merely a white precipitate it is due to the soda and there is no bromide.

If bromine or iodine has been found, the liquid is boiled and air is blown into the tube through a long glass tube drawn out to a point, and inserted almost to the level of the liquid, so as to clear away the vapours from the test-tube. It generally takes about ten insufflations, each preceded by a short boil for the complete expulsion of bromine and iodine. This is ascertained by adding 10 more drops of potassium chromate and boiling. There are then poured in the liquid 20 drops of a solution of permanganate at 5 per cent; the whole is stirred and as much as 1 to 2 c.c. of soda-lye is added with the stirring rod to the surface of the liquid, then into a glass containing aniline water, and stirred, when if chlorine is present we obtain a violet or reddish violet colouration after stirring

* Read at the Chemical Section of the Franklin Institute, November 18, 1890.

for a few moments. It may happen, if there remain traces of bromine, that the colouration will be at first orange, but it will rapidly pass into violet if there is a chloride in the original liquid.

The author has clearly detected the chlorine in a c.c. of a liquid containing:—

	Grm.
KI	0.02
KBr	0.01
NaCl	0.004

He has even been able to detect 1 per cent of sodium chloride in potassium bromide by operating as follows:—

He put into a tube 0.5 grm. pure potassium bromide, and 0.005 grm. sodium chloride, then 40 drops potassium chromate in solution (saturated in the cold), and 30 drops of sulphuric acid. He boiled and blew in air into the tube five or six times. He added, further, 10 drops of the potassium chromate and 10 drops of sulphuric acid. After further boilings and insufflations, he added 20 drops permanganate. The stirring rod, moistened with soda, was left for a quarter of a minute in the lower third part of the tube, and on being then plunged into aniline water it quickly gave a very distinct violet colour.

If we find iodine in the first trial we should not always search directly for bromine in the vapour, because the alkaline hypoiodates give with aniline not, indeed, an orange yellow, but a canary yellow, and a second trial is necessary to detect bromine with certainty.

To this end we put into a tube 1 c.c. of the liquid, 10 drops of ferric chloride, and as much sulphuric acid; the iodine is removed by blowing and boiling; 10 drops of sulphuric acid and 20 drops of potassium chromate are further added, and we test for bromine with aniline water, making use of the stirring rod moistened with soda.

These various reactions necessitate the complete removal of bodies which might mask or enfeeble them, i.e., iodine and bromine in the case of chlorine, and iodine in that of bromine. This is quickly effected by means of boiling and insufflation, but we must not forget that, as in most cases of the analysis of a mixture, we require here a complete separation, very rapid, indeed, and not requiring filtration or distillation, but which must be as complete as possible so as to avoid errors.

This method of analysis founded on the use of glass rods moistened with reagents deserves to be generalised on account of its certainty and facility. The author has indicated its use with isatine and sulphuric acid for the detection of the mercaptans and thiophene, of nitrous vapours by sulphuric acid and diphenylamine sulphate, of ammonia by Nessler's reagent, of sulphurous acid by soda, ferric chloride, and potassium ferricyanide, of sulphuretted hydrogen by soda and sodium nitro-prusside, &c.—*Bulletin de la Société Chimique de Paris.*

ON THE COMPOSITION OF KAOLINIC PORCELAINS.

By M. GEORGES VOGT.

THE analysis of the Chinese and Japanese porcelains has led chemists to conclude that they were composed of kaolin, felspar, and quartz; and according to these analyses it was concluded that the synthesis of Oriental porcelains could be effected by mixing 50 parts kaolin, 30 felspar, and 20 quartz. Upon these data the European porcelain manufacture has been established. If we consider merely the centesimal composition of the various porcelain pastes as deduced from the elementary analysis, this view may seem correct, but if we study them more closely by the procedures of proximate analysis, we are led to perceive that another mineral than those mentioned enters into their composition.

The author has had the opportunity of examining

specimens of the raw materials used in China for the manufacture of porcelain, collected with the utmost care by the late M. Scherzer, Consul at Canton. From the total analysis of the two minerals, yeou-ko and pe-tun, we might be led to consider them as analogous to the pegmatite of Limousin. But on treating pegmatite with sulphuric acid we obtain only 3.3 per cent of soluble matter in place of 34.15 and 40.63 as found in the Chinese minerals.

But if we compare the centesimal composition of the soluble matter of yeou-ko and pe-tun (disregarding in the former the 2.04 of calcium carbonate, and 1.01 silica, which are directly soluble) with that of white mica, there appears such a close similarity that we may pronounce the soluble part found in the Chinese rocks identical in composition with white mica. The mica contained in yeou-ko and pe-tun is in very minute particles, invisible with the naked eye and even with the lens. But a microscopic examination with polarised light detects its presence and confirms the result of the analysis. Hence it appears that the minerals which form Chinese porcelain are distinguished from pegmatite by the presence of a large quantity of mica. The paste used in China in the manufacture of porcelain known as *hoa-che* is an almost pure natural mixture of hydrated aluminium silicate, and white mica in a very fine state of division. The mica found in these Chinese materials must not be confounded with the tablets of ferruginous mica, the presence of which is feared in the preparation of porcelain pastes in Europe.

The mica is first broken up in a disintegrator, then ground with water under porcelain mills, and then levigated in an apparatus with flowing water, so that only the finest portions are collected. These portions are then dried down to a thick consistence. Mica thus prepared possesses a plasticity almost equal to that of kaolin. It can be kneaded, moulded, and it dries without warping or cracking. Under such conditions the introduction of mica into a paste does not in any manner interfere with the ordinary manufacture of the porcelain. In the furnace the mica melts much less easily than felspar, and keeps its form at very high temperatures (1400°). The porcelain paste used in the Imperial manufactory of China is composed of—

Kaolin	23.4
Mica	23.4
Soda-felspar	25.0
Quartz	28.2

On the contrary, the new paste employed at Sèvres consists of—

Kaolin	35.6
Soda and potash felspars	38.0
Quartz	26.4

Total 100.0

The author has endeavoured to reproduce exactly the Chinese porcelain, but found some difficulty in obtaining in France minerals as rich in mica as those of China. He has since found at Montebas (Creuse), a mineral containing 23 per cent of mica, and a kaolin from St. Yrieix containing 20 per cent. The French mica alone is too ferruginous to yield a good paste. A paste composed of—

Kaolin	20
Mica	45
Quartz	40

yielded merely a stone-ware of fine quality. To obtain a beautiful and very transparent porcelain, a certain quantity of felspar must be added, the mixture being—

Kaolin (pure)	25
Mica	25
Orthose	25
Quartz	20

A paste containing 17 per cent of mica yielded by the following mixture—

Kaolin, containing 20 per cent of mica ..	35
Montebraz mineral (23 per cent of mica) ..	57
Orthose	20

yielded a fine porcelain of great whiteness. These porcelains, although baked at 1450°, can be covered with alkaline glazes in the furnace and with enamels in the muffle.—*Bulletin de la Société Chimique de Paris.*

THE DRY ASSAY OF TIN ORES.*

PART II.

By HEINRICH O. HOFFMANN,
Assistant Professor of Mining and Metallurgy.

(Concluded from p. 302).

VI. Preparation of the Ore for the Assay.

It will be seen from the foregoing that the influence of the associated minerals on the result of the assay is very considerable. It becomes, therefore, necessary to have as pure a black tin as possible for the dry assay. When it is remembered that tin ores contain only from 0.75 to 3 per cent of cassiterite, their preparation for the assay is seen to be a very important part of the work.

The separation of the cassiterite from the gangue is accomplished by crushing and washing. The resulting concentrates are then purified by means which vary according to circumstances. From the great difference in specific gravity between the cassiterite (6.4 to 7.1) and the non-metallic associated minerals (not over 4.1), it would appear at first sight that the separation ought to be very easy, but this for various reasons is far from being the case. Special precautions are needed if the loss of black tin is to be reduced to a minimum. The metalliferous minerals have too great a specific gravity (e.g., arsenopyrite 6 to 6.4) to be removed by washing; roasting and acids have to be used. The columbite (tantallite), whose specific gravity varies from 5.89 to 6.12, remains finally with the black tin, as it is not attacked by ordinary acids at all.

The implements used in assay laboratories for pulverising larger quantities of ore are a small hand-crusher and a pulverising plate. The ore is usually crushed, sampled down, and then pulverised on the rubbing-plate or in a mortar. Experience has proved that the common method of grinding the whole sample to a uniform size is not suited to the tin ores of the Black Hills. The main reason for this is the preponderance of mica. Anyone who has tried to pulverise mica, even if previously heated, will appreciate the difficulty. Happily, very little cassiterite occurs in the mica proper, which if ground for a short time only on the rubbing-plate will not show any black tin or other mineral. The pulverisation must be carried on with the subsequent washing in view. The first rule in concentration is, that a good preliminary sizing should precede the separation by specific gravity. The second is, that the ore should be coarse, to prevent loss in washing. The latter point is strongly emphasized in the present case by the fact that the brittle cassiterite will be ground to a slime, while other minerals in the ore are only converted into sands. The writer's practice has been to screen while the ore is being pulverised, crushing and screening alternately with a graduated series of sieves, Nos. 20, 40, 60, and 80. The ore is crushed until all the minerals, with the exception of the mica, are fine enough to pass a 20-mesh sieve; the mica is then examined for any minerals adhering to it, and these are removed by grinding, and screened. The different screenings are now washed separately in the gold pad, and the tailings panned over. The concentrates obtained by the separate washings are put together, dried,

and passed through a 60-mesh sieve, and the washing is repeated, the result being pure concentrates and tailings. These are panned over if any cassiterite appears.

The writer has done all his washings of tin ore in the gold pan; but any other apparatus, be it the vanning shovel used in Cornwall, or the "Sichertrog" of the Saxon or Bohemian miner, will, with the necessary practice, give the same result. In panning, it is found very difficult to separate the cassiterite from the garnet without losing much tin, although there is a great difference in their specific gravities, viz., 6.4 to 7.1 and 4.1. It is almost impossible to effect a complete separation, as can be seen from the analysis of the average sample, where the insoluble residue, 9.39 per cent, is principally garnet. This is on account of the different way in which the minerals break. Dana† says that both cassiterite and garnet have an uneven, subconchoidal fracture, and that both are brittle; they also differ little in hardness (6 to 7 vs. 6.5 to 7.5). But the cassiterite crushes into splinters, and the garnet into a granular form. It is probably this difference that causes the difficulty in separating the two minerals; the preponderating particles of cassiterite form an irregular angular network, and prevent the heavy garnet from being carried off by the water with the other minerals that have a lower specific gravity. If garnets are present in any large quantities it will be necessary to adopt other means to remove them. Dana‡ says that all garnets, except ouvarovite, are decomposed with hydrochloric acid after ignition. That this may be complete, the mineral has to be ground very fine. It will be remembered that the black tin used for the experiments was roasted, chilled, and treated with nitro-hydrochloric acid, and the garnets were not entirely removed. If the garnet is decomposed, the removal of the gelatinous silica, either by washing or by hydrofluoric acid, is simple.

The black tin obtained by washing still retains sulphides and arsenides. Berthier§ recommended boiling with nitro-hydrochloric acid, and burning off any sulphur that might have separated. Plattner¶ objects to this, as the sulphur would not all be eliminated. He reverses the process, roasting first and then treating with nitro-hydrochloric acid. Following Plattner, the black tin is roasted on a dish in a muffle, and, to assist the decomposition of the garnet, chilled in cold water after roasting; it is then boiled in a porcelain dish with nitro-hydrochloric acid, which will also remove particles of metallic iron coming from the implements used in grinding; when all the iron is dissolved, the solution is poured off, and any light particles washed away. If necessary, the concentrates can be transferred to a platinum dish and treated with hydrofluoric acid. This, however, will rarely be required.

The roasting seems to have a favourable effect on the cassiterite by making it more friable and more readily reducible. The unroasted cassiterite of the Black Hills is subtranslucent, brown to black, and very hard to pulverise; the roasted mineral is opaque, of a more or less reddish brown, and easily pulverised. The change that takes place in the reducibility of the ore is shown by the following experiments:—

TABLE XXVIII.

No. of assay.	Name of mine.	Per cent of tin from raw ore.	Per cent of tin from roasted ore.
168.	Occidental	48.90	49.00
169.	Glendale	65.30	65.60
170.	First Find	65.30	65.80
171.	Similias	75.00	75.00

The results show that in some cases (No. 171) no difference exists between raw and roasted concentrates, while in others it may amount to 0.5 per cent.

* Read at the Colorado Meeting of the American Institute of Mining Engineers, June, 1889. From the *Technology Quarterly*, Vol. iii., No. 3.

† "System of Mineralogy," 5th ed., New York, 1880, pp. 158 and 265.

‡ *Op. cit.* p. 270.

§ "Traité des Essais," 1847, vol. ii., pp. 486, 487.

¶ "Blowpipe Analysis," edited by Richter, and translated by Cornwall, New York, 1885, p. 466.

If the preliminary treatment of the tin ore is carried out in the manner described there will be a minimum of loss in black tin.

VII. Conclusion.

From this examination of the different methods of assaying tin ores in the dry way, it becomes apparent that, if ordinary precautions are taken, the necessary treatment, including the preliminary preparation of the ore, is a comparatively simple matter; neither is the influence of the associated minerals so great, at least with the cyanide assay, as is generally supposed. Lastly, the results obtained show that the dry assay of purified black tin gives more accurate results than that of any other base metal, if the few correct methods, none of them requiring special skill, are followed and ordinary care is given to the work.

THE COEFFICIENT OF MINERAL CONDENSATION IN CHEMISTRY.*

By T. STERRY HUNT.

(Concluded from p. 306).

19. THE history of the development of this modern conception in chemistry is one of such importance as to demand a somewhat extended study. The earliest statement, so far as the writer is aware, of the application of the doctrine of complex formulae, of high equivalent weights, and of homologous relations (already recognised among hydrocarbonaceous bodies in the domain of organic chemistry), to mineral, or inorganic, chemistry will be found in a paper by him in 1853. Therein it was contended that isomorphous solid species, at least, "have the same equivalent volume, so that their equivalent weights (as in the case of vapours) are directly as their densities; and the equivalents of mineral species are as much more elevated than those of the carbon series as their specific gravities are higher." Referring to the latter, "the hydrocarbonaceous, or so-called organic, species," and to the law of progressive or homologous series therein first pointed out by James Schiel, of St. Louis, and soon after adopted by Charles Gerhardt, it was said that, it may be expected that mineral species will exhibit the same general relations as those of the carbon series, and the principle of homology be greatly extended in its application. The history of mineral species affords many instances of isomorphous silicates, whose formulae differ by $n(\text{O}_2\text{M}_2)$, as the tourmalines, and the silicates of alumina and of magnesia.

It was then further declared that the native mineral carbonates or carbon-spars must be represented as polycarbonates having not less than from "twelve to eighteen equivalents of base replaceable so as to give rise to a great number of species"; among which the relations of their densities were said to "indicate the existence of several homologous genera which are isomorphous." In subsequent papers, in 1853 and 1854, attempts were made to show that in these polycarbonates, $n(\text{CMO}_3)$, the different values of n might be not less than 22, 25, 30, 36, and 40. Similar elevated formulae were also given in 1853 for various polysilicates, as in the cases of augite, amphibole, and wollastonite, and of the feldspars, albite, anorthite, and orthoclase. In this connection the complex silicates containing chlorides, carbonates, and sulphates were considered and compared to basic salts.†

* From the *American Chemical Journal* for November, 1890, vol. xii., No. 8.

† "The Theory of Chemical Changes and Equivalent Volumes," *Am. J. Sci.*, xv., (226-234); *Phil. Mag.* (4) v., 326; and in a German translation in the *Chem. Centrbl.* of Leipzig for the same year (p. 849); also in the author's "Chem. and Geol. Essays," pp. 427-437. Further, "The Constitution and Equivalent Volume of Mineral Species," *Am. J. Sci.*, xvi., (203-218), and in abstract, in the author's "Chem. and Geol. Essays," p. 435, &c. Also, "Illustrations of Chemical Homology," *Proc. Am. Assn. Adv. Sci.*, 1854, pp. (237-247); also, in abstract, *Am. J. Sci.* for September of the same

The variations in the ratios of silica and alumina in nearly related species, and the apparent partial replacement therein of silica by the latter, then imperfectly understood, were noted in 1854 as seeming to invalidate the distinction between silica, as the negative or acidic member, and the positive or basylous member of these oxidised compounds, in which alumina was at that time still included.

20. These views of polymerism in mineral species, involving on the one hand the conception of many equivalents of replaceable base, and on the other of many equivalents of the acidic or negative element, which might be either carbonic, silicic, or boric oxide, or might include with the latter alumina, sulphates, carbonates, or fluorides, though thus enunciated in 1853, found no favour among chemists until 1860, when Adolphe Wurtz again put forth the notion of polysilicates, citing in connection therewith the metastannates of Frémy, in which the negative element consists of $5(\text{SnO}_2)$. The similar metatungstates or tetratungstates, the pyroborates, the polyphosphates of Fleitman and Henneberg, including tetraphosphates and dekaphosphates, and the not less complex phosphates of Wallroth, with $9(\text{P}_2\text{O}_5)$, soon showed that such a polymerism is not exceptional in negative or acidic oxides. The studies of other chemists, moreover, made it known that similar compounds, including different negative oxides of the same or of unlike valencies, were not less frequent; as appears in the complex phosphovanadates and arsenovanadates, in the aluminomolybdates, the ferrimolybdates, the borotungstates, the silicotungstates, the phosphotungstates, the phosphomolybdates, the stannophosphomolybdates, and salts of still greater complexity and of very high equivalent; often presenting series which illustrate in a striking manner the extension to such mineral species of the law of progressive series.

The high integral weight, the limited basicity, and the partial instability of these complex salts are well illustrated in the phosphomolybdate of ammonia formed in the ordinary method for determining phosphorus thereby. This insoluble compound, when precipitated in presence of an excess of chlorhydric or nitric acid, contains $12\text{MoO}_3 \cdot \text{PO}_4 \cdot (\text{NH}_4)_3$, besides $2\text{NO}_3 \cdot \text{H}_2\text{O}$ or $2\text{HCl} \cdot \text{H}_2\text{O}$, constituting a nitro-, or a chlorhydro-, phosphododekamolybdate; but by desiccation at 150° these volatile acids and water are expelled, leaving the phosphomolybdate with 3.78 per cent of phosphoric oxide, P_2O_5 .

21. We have thus endeavoured to trace the steps by which, from the writer's first enunciation, in 1853, of complex formulae, high integral weights, and homologous, or progressive, series in mineral species, chemists have been led up to the comprehensive generalisation which Wolcott Gibbs has embodied in the important conception of what he has called complex inorganic acids. The results of chemical analysis, while they permit us in many instances to assign small integral weights to chemical species, force us to conclude that in other instances these integral weights are very elevated, conclusions which in the one and in the other case are confirmed alike by the vapour-density and by the cryoscopic method; which latter it will be desirable to verify still further by the study of many soluble salts of apparently complex constitution.

22. The cases which we have just considered show in chemical species of related centesimal composition, as in formaldehyd, xylose, glucose, the higher sugars, the dextrines and soluble starch, integral weights rising from 30, 150, and 180 to numbers which cannot be less than thousands. These figures suggest for chemical species a range of integral weights which may conceivably rise to that of the mineral species itself. Instead of being, as in glucose and other sugars, a multiple of the chemical integer by a high number, the coefficient for the mineral

year; and noticed, with extracts, in the author's "Chem. and Geol. Essays," p. 438 et seq. The whole question is further discussed in the author's "Mineral Physiology, &c.," pp. 288-295.

species becomes a small one, as in the case of the dextrines and soluble starch, or of the cobaltamines and the polytungstates. So far as is yet known, however, there intervenes, in all cases, a greater or less polymerisation, the study of which will be found to have important thermochemical relations.

If we consider the four groups of sugars represented chemically by xylose and arabinose (C_5), glucose (C_6), saccharose (C_{12}), and raffinose (C_{18}), but having for the mineral species essentially the same specific gravity, assumed to be 1.5, we shall have for the coefficients of the mineral species, respectively, the numbers 214, 180, 94, and 54, corresponding to a common integral weight, therefore, of 32,100; xylose being $214(C_5H_{10}O_5)$, glucose $180(C_6H_{12}O_6)$, &c. In the case of the volatile polymeric hydrocarbons already mentioned (§8), α -decylene (CH_2)₁₈, cerotene (CH_2)₂₇, and melene (CH_2)₃₀, assuming the specific gravities assigned for the solids, namely, 0.79, 0.86, and 0.89, to be correct, we have respectively the coefficients for the solid mineral species of 67, 48, and 45. Melene will be $45(CH_2)_{30}$, cerotene $48(CH_2)_{27}$, and α -decylene $67(CH_2)_{18}$.

23. The ammonio-cobalt salts, from the results of chemical analysis, have necessarily high integral weights for the chemical species, and have assigned to them densities of about 1.7–1.8; the former figure corresponding to an integral weight for the mineral species of about 36,380.* The minimum chemical weight for the orthometaphosphate of luteocobalt (=2540) would demand a coefficient for the mineral species of 14, since $14 \times 2540 = 35,560$. In like manner the soluble crystalline hydrous polyphosphotungstates have for sodium salts, according to Scheibler, specific gravities of 3.84–3.98, and for a barium salt 4.3. I find no determination of specific gravity for the highly complex polyphosphovanadate (§1) to which Gibbs assigns a chemical weight of 20,058, and which, should its coefficient of polymerisation be 4, would have a specific gravity of 3.75, nearly. More or less uncertainty must, however, still exist with regard to the true chemical formulæ, and consequently to the integral weights of chemical species of such complex constitution as those now under consideration. Under the name of tungsten-bronzes have been conveniently included several anhydrous crystalline bodies, metallic in lustre, conductors of electricity and highly electro-negative, which are nevertheless oxidised compounds of tungsten and an alkali-metal. The tungsten-bronze first described by Wöhler is, in the opinion of Gibbs, probably $16WO_3 \cdot 4WO_2 \cdot 7Na_2O (=5002)$. To this has been assigned a specific gravity of 6.617; to another sodium species, 7.28; and to a potassium species, 7.60.

24. The fact that in the soluble hydrous polytungstates, hydrocarbon radicles like methyl, ethyl, and phenyl may enter, helps to break down the barrier, not yet wholly removed, which once separated the so-called organic and inorganic compounds (§2). Even the stability of insoluble silicates is not proof against similar changes, as shown in the case of artificial ultramarine. This, which is got as a blue, green, or violet crystalline powder, appears to be essentially a peculiar sodium aluminosilicate in which the oxygen is partially replaced by sulphur. By digestion with a solution of silver nitrate a yellow substance is got in which silver replaces sodium, and this with ethyl iodide yields a compound into which the alcohol radicle enters, and which by subsequent treatment with sodium chloride gives off ethyl chloride and regenerates blue ultramarine. The silver in the yellow species may also be replaced by potassium or by lithium, the last giving also a blue ultra-

marine. Similar compounds are obtained from ultramarine* the iodides of amyl, allyl, and benzyl.* It is probable that only their great insolubility prevents us from getting somewhat similar results with more highly condensed silicates, such as the felspars, micas, and tourmalines.

25. It will be clear to those who have followed the preceding argument, that in cases where neither the vapour-density nor the cryoscopic method can be evoked, that is to say in non-volatile and insoluble mineral species, we have not the means of determining the integral weight of the chemical species which by its subsequent condensation generates such mineral species; or of discovering whether this may have attained that condensation by a single step or by successive stages. Thus, by hypothesis, a solid like retene might be generated directly by the intrinsic condensation of acetylene, or from benzene; the production of the latter hydrocarbon marking an intermediate stage in the progress of homogeneous integration. What stages, if any, intervene in the passage from the soluble normal calcium carbonate to the insoluble crystalline mineral species, calcite and aragonite, we may never know, though from the existence of these two mineral species of identical centesimal composition with different degrees of condensation and of solubility in acids, corresponding to the differences observed in the various polymers of many hydrocarbons, aldehydes, &c., we may with great probability suspect the existence of intermediate and unstable stages of condensation in calcium carbonate. The same argument applies equally to the unlike forms of silicon dioxide, tridymite, and quartz, differing alike in specific gravity and in solubility; to the two forms of iron disulphide; and to other cases too many to recall.

26. We can in very many cases recognise at least two distinct stages of polymerisation in the passage of a given chemical species, either simple or compound, into a mineral species. The first stage is seen when the vapour of sulphur (S_2) passes by intrinsic condensation into the denser vapour (S_6); gaseous acetylene into the vapour of benzene, of cinnamene, or of retene; or when formaldehyde dissolved in water is changed to an aqueous solution of formose. The second stage is seen in the passage of the dense sulphur vapour, the polymerised hydrocarbon vapours, or the dissolved formose, into liquid or solid forms. For the great multitude of mineral species of which the corresponding volatile or soluble species are unknown to us, the means of marking these separate stages are wanting, and we have but two data: the specific gravity of the mineral species, water being unity, and the equivalent weight as deduced from the results of chemical analysis; d = the specific gravity and p = the equivalent weight. The latter, for compound species, may be calculated from the simplest formula which represents intelligibly the results of such analysis,—or, as we have elsewhere proposed as the basis of a wider comparison which should include all metallic oxides, salts, and haloid compounds—by the adoption for p of a still simpler and an arbitrary unit. For all such species “we assume as the unit for p a weight including that of $H=1$, of $Cl=35.5$, or of $O \div 2=8$. By thus adopting a combining weight of 8.0 for oxygen, we get a unit which gives a common term of comparison for oxides, sulphides, chlorides, fluorides, and for intermediate compounds like the oxysulphides and oxyfluorides common in native species.” For all silicates, carbonates, sulphates, phosphates, and more complex species, we find the value for p “by dividing in all cases the empirical equivalent weight by twice the number of oxygen portions ($O=16$ plus the number of chlorine or fluorine portions.”† This

* The revision by Crafts in 1888 of Regnault's determination of the weight of a litre of hydrogen in the latitude of Paris, making it 0.08988 grm. (instead of 0.08975 grm.) gives—if $O=15.06$ —for the integral weight of water 21,335 in place of 21,406. In the uncertainty which still prevails as to the precise value of oxygen as compared with hydrogen, we may yet retain for water—the unit of specific gravity for liquids and solids—the number hitherto adopted, 21,400, as a close approximation, since the difference would only involve an error of about three-thousandths of a unit in such specific gravities.

* For a summary of the results of the study of ultramarine by Neumann, Philipp, and de Forcrand, see “Watts's Dict. Chem.,” 3rd Suppl., 2069–2071.

† For a further discussion of this question see the author on Chemical Integration in *Am. J. Sci.* for August, and in *Chem. News*, lvi., 136, 142; also his volume, “A New Basis for Chemistry,” 1888, 2nd ed., pp. 225–227, and a French translation thereof by Prof. W. Spring, with additions by the author, entitled “Un Systeme Chimique Nouveau,” Paris, 1889.

method was already adopted by the author in 1886, and he has since proposed to complete it by the device of a notation as near as may be monadic, in which, by the use of various kinds of type, the valencies of the combining elements are made apparent.*

27. Since the arbitrary mean chemical unit ρ , thus assumed, represents in all cases an aliquot part of the chemical species, however simple or however complex, which by its final intrinsic condensation has generated the mineral species whose specific gravity ($=d$) is known, it follows that the equation $\rho + d = v$, giving in v the reciprocal of the coefficient of condensation, permits a ready comparison of the relative condensation in mineral species, upon which, as we have elsewhere endeavoured to show, the hardness and the chemical indifference of solids depend.

It will be remembered that ρ , which represents the equivalent weight of the chemical unit, corresponds in the last analysis to the specific gravity of that unit presumed to be gaseous,—hydrogen gas at standard temperature and pressure being unity ($H=1$),—while d represents the specific gravity of the liquid or solid mineral species, liquid water at its point of condensation at standard pressure being unity ($I=21,400$). The value deduced from this conventional ρ is readily adapted to any rational formula which may be admitted for the species in question. Thus quartz, represented as silicon dioxide, $SiO_2=60+4=15=\rho$, and this being divided by 2.65, the specific gravity of quartz, we find $v=5.66$, which for SiO_2 gives $v=22.64$. We have then the proportion—

$$22.64 : 21,400 :: 1 : 945.$$

In other words, if simple silicon dioxide passes directly into the mineral species quartz, the coefficient of condensation is approximately 945, or perhaps 950 (SiO_2). Should it be found, as is probable, that silicon dioxide in its soluble colloidal condition is a polymer of greater or less equivalent weight, represented by $(SiO_2)_{10}$ or by $(SiO_2)_{50}$, the above coefficient therefor would be divided by these numbers: the total coefficient of mineral condensation, comprising two or even more stages, being in each case the same. In the application of Raoult's method to colloidal silica, the reduction of the freezing point, according to Sabaneff, was so slight that the values all came within the limits of errors of observation,† as would also appear to be the case with soluble starch.

To take another example, calcite—

$$CCaO_3 = 100 + 6 = 106 = \rho.$$

Dividing ρ by 2.73, as the specific gravity of calcite, we find $v=6.10$ nearly, which for $CCaO_3$ gives $v=36.6$.

$$36.6 : 21,400 :: 1 : 584.$$

The condensation from $CCaO_3$ to calcite of specific gravity 2.73 is thus represented by 584 ($CCaO_3$). Here, too, as in the case of silicon dioxide, it is probable that there exists an intermediate polymer, represented by a soluble form of carbonate of lime, long since noticed by the writer.‡

28. These numbers thus arrived at for quartz and for calcite are, of course, but approximations, since the exact equivalent weights of oxygen and of silicon are still uncertain, and since, moreover, there are small variations in the specific gravity of the mineral species themselves, from which Breithaupt with much plausibility conjectured, in the case of calcite, the existence of several species, rhombohedral in form, with specific gravities

* See in the author's "Mineral Physiology and Physiography" an essay on "A Natural System of Mineralogy, with a Classification of Silicates; and later, "Notes on Valency, Basicity, Complex Acids, and Chemical Notation: CH. M. N. W. S., lxi., 267.

† *Am. J. Sci.* (III.), xl., 87.

‡ Recently-precipitated and still gelatinous calcium carbonate is soluble in water containing small quantities of calcium chloride or of magnesium sulphate, a litre at ordinary temperatures holding for many hours a gram or more of the dissolved carbonate, which, however, finally separates completely in transparent hydrated crystals, $CCaO_3 \cdot 5H_2O$. See the "History of Lime and Magnesia Salts," *Am. J. Sci.*, 1866, (2), xlii., 58, 59; also "Mineral Physiology, &c.," p. 168.

ranging from 2.652 to 2.754. At the same time we must not overlook the calcium carbonate, aragonite, harder and less soluble in acids, with a specific gravity of 2.94, showing a higher intrinsic condensation than any calcite.

We have spoken of the views advanced in this paper as based on an hypothesis. It is, however, an hypothesis founded on a belief in the universality and the invariability of the law of volumes, and one which appears to be in complete harmony with the facts of chemistry so far observed. As one of the conclusions of a lifetime devoted to the study of certain chemical problems discussed more at length in the later editions of his "New Basis for Chemistry," the writer now submits his paper to the judgment of philosophers.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

December 12, 1890.

Prof. W. E. AYRTON, F.R.S., President, in the chair.

SHELFORD BIDWELL, F.R.S., showed "Some Experiments with Selenium Cells."

The crystalline variety of selenium was, he said, most interesting to physicists owing to its electrical resistance being greatly diminished by light. This property was shown experimentally with different forms of cells, the construction of which were explained. The form recommended was that in which two copper wires are wound near each other round a slip of mica, and the spaces between the wires filled with selenium. The wires form the terminals of the so-called "cell," which, before being used, is annealed for several hours at a temperature above 200° C. Many such cells were made in 1880 and 1881, and their sensitiveness to light remained unimpaired during 1882. In 1885, however, several were found less sensitive, and others totally useless; only one out of thirteen retained its sensibility till September, 1890. The loss of sensitiveness, Mr. Bidwell believes due to an excessive amount of selenide of copper being formed, for although some selenide is essential to the satisfactory working of the cell, too much is fatal to its action. The selenide of one defective cell was electrolysed, red tufts of amorphous selenium appearing on the anodes. A white substance resembling moist calcium chloride was also present; this he believed to be oxide or hydroxide of selenium. Small polarisation currents had been obtained from selenium cells.

A lecture apparatus illustrating the properties of selenium cell was exhibited. It consisted of a cell connected in series with a relay and a battery. The relay was arranged so that it might either ring a bell or light an incandescent lamp. When the bell was joined up, it remained silent so long as the selenium cell was illuminated, but on screening the cell the bell rang. By using various coloured glasses as screens, the effect was shown to be due to the red and yellow rays. A similar experiment with the glow-lamp was very striking, for on turning down the gas-lamp illuminating the cell, the electric lamp lighted, and was extinguished on turning up the gas. This demonstrated the possibility of an automatic lamp-lighter which would light or put out lamps according as they are required or are superfluous. Amongst the other practical applications suggested were, announcing the accidental extinction of railway-signal lamps or ship's lights, and the protection of safes and strong-rooms.

Prof. MINCHIN said he had lately constructed cells of a different kind to those shown by Mr. Bidwell, and found that they gave an E.M.F. when exposed to light. For his purposes the long annealing, &c., were quite unnecessary,

and a complete cell could be made in ten minutes. One of his cells gave an E.M.F. of over 0.25 volt, as measured by an electrometer, by the light of a fog. Their promptness of action falls off in a day or two, but if they are kept on open circuit a week has no effect on the final E.M.F. On closed circuit, however, they deteriorate.

Prof. S. U. PICKERING said both oxides of selenium were deliquescent, and the author's conclusion as to the white substance formed by electrolysis was probably correct.

Prof. S. P. THOMPSON believed Prof. Graham Bell had tried platinum instead of copper, and found that the selenium cracked off in annealing. He also found that it was only necessary to carry on the annealing until the characteristic slate colour appeared. Mr. Bidwell's experiments, he said, showed the possibility of seeing at a distance, and had also suggested to him that the effect of screening might be utilised for driving a completely detached pendulum electrically.

Prof. FORBES said that silver sulphide when electrolysed presented appearances resembling those noticed by Mr. Bidwell in copper selenide.

In reply to questions from the President and Prof. Perry as to whether the low resistance and unsensitiveness of old cells was due to moisture, Mr. Bidwell said, drying them had no effect, but baking restored the resistance, but not their sensitiveness. Speaking of the effect of annealing cells, he said this reduced their resistance considerably. Prof. Graham Bell, he believed, gave up using platinum because the resistances of such cells were very high.

Mr. JAMES SWINBURNE read a paper on "*Alternate Current Condensers.*"

It is, he said, generally assumed that there is no difficulty in making commercial condensers for high pressure alternating currents. The first difficulty is insulation, for the dielectric must be very thin, else the volume of the condenser is too great. Some dielectrics, 0.2 m.m. thick, can be made to stand up to 8000 volts when in small pieces, but in complete condensers a much greater margin must be allowed. Another difficulty arises from absorption, and whenever this occurs the apparent capacity is greater than the calculated. Supposing the fibres of paper in a paper condenser to be conductors embedded in insulating hydrocarbon, then every time the condenser is charged the fibres have their ends at different potentials, so a current passes to equalise them and energy is lost. This current increases the capacity. One condenser made of paper boiled in ozokerite took an abnormally large current and heated rapidly. At a high temperature it gave off water, and the power wasted and current taken gradually decreased.

When a thin plate of mica is put between tin foils, it heats excessively; and the fall of potential over the air films separating the mica and foil is great enough to cause disruptive discharge to the surface of the mica. There appears to be a luminous layer of minute sparks under the foils, and there is a strong smell of ozone.

In a dielectric which heats, there may be three kinds of conduction, viz., metallic, when an ordinary conductor is embedded in an insulator; disruptive, as probably occurs in the case of mica; and electrolytic, which might occur in glass. In a transparent dielectric the conduction must be either electrolytic or disruptive, otherwise light vibrations would be damped.

The dielectric loss in a cable may be serious. Calculating from the waste in a condenser made of paper soaked in hot ozokerite, the loss in one of the Deptford mains came out 7000 Watts. Another effect observed at Deptford is a rise of pressure in the mains. There is as yet no authoritative statement as to exactly what happens, and it is generally assumed that the effect depends on the relation of capacity to self-induction and is a sort of resonator action. This would need a large self-induction, and a small change of speed would stop the effect. The following explanation is suggested. When a condenser is put on a

dynamo, the condenser current leads relatively to the electromotive force, and therefore strengthens the field magnets and increases the pressure. In order to test this, the following experiment was made for the author by Mr. W. F. BOUNE. A Gramme alternator was coupled to the low pressure coil of a transformer, and a hot-wire voltmeter put across the primary circuit. On putting a condenser on the high pressure circuit the voltmeter wire fused. The possibility of making an alternator excite itself like a series machine, by putting a condenser on it, is pointed out.

Prof. PERRY said it would seem possible to obtain energy from an alternator without exciting the magnets independently, the field being altogether due to the armature currents.

Mr. SWINBURNE remarked that this could be done by making the rotating magnets a star-shaped mass of iron.

Sir W. THOMSON thought Mr. Swinburne's estimate of the loss in the Deptford mains was rather high. He himself had calculated the power spent in charging them, and found it to be about 16 horse power, and although a considerable fraction might be lost, it would not amount to nine-sixteenths. He was surprised to hear that glass condensers heated, and inquired whether this heating was due to flashes passing between the foil and the glass.

Mr. A. P. TROTTER said Mr. Ferranti informed him that the capacity of his mains was about $\frac{1}{4}$ microfarad per mile, thus making $2\frac{1}{2}$ m.f.s. for the seven miles. The heaping up of the potential only took place when transformers were used, and not when the dynamos were connected direct. In the former case the increase of volts was proportional to the length of main used, and 8500 at Deptford gave 10,000 at London.

Mr. BLAKESLEY described a simple method of determining the loss of power in a condenser by the use of three electro-dynamometers, one of which has its coils separate. Of these coils one is put in the condenser circuit and the other in series with a non-inductive resistance, r , shunting the condenser. If a_2 be the reading of a dynamometer in the shunt circuit, and a_3 that of the divided dynamometer, the power lost is given by $r(Ca_3 - Ba_2)$, where B and C are the constants of the instruments on which a_2 and a_3 are the respective readings.

Prof. S. P. THOMPSON asked if Mr. Swinburne had found any dielectric which had no absorption. So far as he was aware pure quartz crystal was the only substance.

Prof. FORBES said Dr. Hopkinson had found a glass which showed none.

Sir W. THOMSON, referring to the same subject, said that many years ago he made some tests on glass bottles which showed no appreciable absorption. Sulphuric acid was used for the coatings, and he found them to be completely discharged by an instantaneous contact of two balls; the duration of contact would, according to some remarkable mathematical work done by Hertz in 1882, be about 0.0004 second, and even this short time sufficed to discharge them completely. On the other hand, Leyden jars with tinfoil coatings showed considerable absorption, and this he thought due to want of close contact between the foil and the glass. To test this he suggested that mercury coatings be tried.

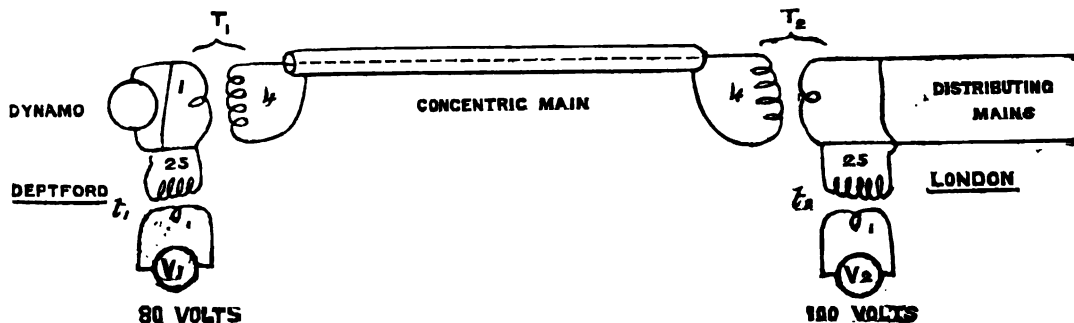
Mr. KAPP considered the loss of power in condensers due to two causes: first, that due to the charge soaking in; and second, to imperfect elasticity of the dielectric. Speaking of the extraordinary rise of pressure on the Deptford mains, he said he had observed similar effects with other cables. In his experiments the sparking distance of a 14000 volt transformer was increased from $\frac{1}{4}$ of an inch to 1 inch by connecting the cables to its terminals. No difference was detected between the sparking distances at the two ends of the cable, nor was any rise of pressure observed when the cables were joined direct on the dynamo. In his opinion the rise was due to some kind of resonance, and would be a maximum for some particular frequency.

Mr. MORDEY mentioned a peculiar phenomenon ob-

served in the manufacture of his alternators. Each coil was tested to double the pressure of the complete dynamo, but when they were all fitted together their insulation broke down at the same volts. The difficulty had been overcome by making the separate coils to stand much higher pressures.

Prof. RÜCKER called attention to the fact that dielectrics alter in volume under electric stress, and said that if the material was imperfectly elastic, some loss would result.

The PRESIDENT said that as some doubt existed as to what Mr. Ferranti had actually observed, he would illustrate the arrangements by a diagram.



Explanation of Diagram:— T_1 and T_2 are large transformers; t_1 and t_2 are small transformers for voltmeters V_1 and V_2 ; the numbers 1, 4, 1, 25, represent their conversion ratios.

Speaking of condensers he said he had recently tried plates in water to get large capacities, but so far had not been successful.

Mr. SWINBURNE, in replying, said he had not made a perfect condenser yet, for although he had some which did not heat much, they made a great noise. He did not see how the rise of pressure observed by Mr. Ferranti and Mr. Kapp could be due to resonance. Mr. Kapp's experiment was not conclusive, for the length of spark is not an accurate measure of electromotive force. As regards Mr. Mordey's observation, he thought the action explicable on the theory of the leading condenser current acting on the field magnets. The same explanation is also applicable to the Deptford case, for when the dynamo is direct on, the condenser current is about 10 amperes, and this exerts only a small influence on the strongly magnetised magnets. When transformers are used the field magnets are weak, whilst the condenser current rises to 40 amperes.

Mr. Blakesley's method of determining losses was, he said, inapplicable, except where the currents were sine functions of the time, and consequently could not be used to determine loss due to hysteresis in iron, or in a transparent dielectric.

Mr. Swinburne's "Note on Electrolysis" was postponed till next meeting.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxi., No. 23, December 8, 1890.

On Allyl Fluoride.—H. Meslans.—The author pours drop by drop allyl iodide upon dry silver fluoride contained in a small copper flask fitted with an ascending

condenser. The flask is kept in water at 35° , and the worm is cooled to 2° or 3° . The gas traverses a tube of silver fluoride, heated to 60° , which arrests allyl iodide, and is collected over mercury. Allyl fluoride is a colourless gas with an odour of garlic and a burning taste. It is easily ignited and burns with a smoky flame, giving off vapours of hydrofluoric acid. If cooled to 1° it is liquefied at a pressure of 760 m.m. Water dissolves 24 vols. of this gas at 15° , alcohol dissolves 60 vols., and ether 100 vols. Its specific gravity taken at 16° is in the mean 2.11, theory requiring 2.10. Its composition is C_3H_5F .

On some Endothermic and Exothermic Reactions of the Organic Alkalies.—Albert Colson.—The author compares diisobutylamine with the alkaline earths. The formation of a molecule of barium oxalate evolves 5.6 cal.; that of a molecule of diisobutylamine oxalate 6.5 cal.

On Certain Derivatives of Dimethylaniline.—Chas. Lauth.—Dimethylaniline if submitted to the action of various oxidising agents forms Paris violet. If lead peroxide is used as the oxidising agent the product is tetramethylbenzidine, $C_{16}H_{20}N_2$. The nucleus, C_6H_5 , is attacked, whilst in the formation of Paris violet the group CH_3 is oxidised and yields the methanic carbon necessary for the development of this colouring matter.

Revue Générale des Sciences Pures et Appliquées.
Vol. i., No. 21, November 15, 1890.

A New Type of Chemical Compound: Nickel Tetracarbonyl.—L. Mond, Carl Langer, and F. Quincke.—This memoir is found in the *CHEMICAL NEWS*, vol. lxii., p. 97. The authors are here described as three English chemists.

Discovery of Free Fluorine in Nature.—MM. Becquerel and Moisson.—Noticed under *Comptes Rendus*.

No. 22, November 30, 1890.

The Probable Cause of the Actino-electric Phenomena.—H.H. Lenard and Wolf, examining certain phenomena by Hertz and by Nodon, find that the ultra-violet light pulverises certain bodies, and that electricity is carried off by particles torn from their surface. Some metals, copper in particular, are very decidedly comminuted under the influence of the ultra-violet light.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xi., No. 2.

On the Spontaneous Combustion of Coal.—Prof. Lewes.—A paper read before the Institution of Naval Architects.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. v., No. 57.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. iv., No. 8.

Bleaching Bees'-Wax and Composition of White Wax.—A. and P. Buisine.—Wax is most frequently bleached by simple exposure in thin shavings to air and light, especially to the direct rays of the sun. In the dark it is not decolorised even in a current of strongly ozonised oxygen. In air-bleaching pure yellow waxes lose only from 1 to 2 per cent of their weight; the melting-point remains sensibly the same; there are formed mere traces of acids soluble in water; the free and combined acids remain within the limits fixed for yellow waxes. The quantity of carbides is decreased, and the "iodine figure" is lowered about by one half. In practice from 3 to 5 per cent of tallow is always added to yellow wax before bleaching. The chief reason for this addition is that pure air-bleached wax is too brittle. With the addition of tallow the bleaching is more rapid, and the furnished product is whiter. The oleic acid contained in the tallow assists in the combustion of the colouring matters. Oil of turpentine added in small quantity acts in the same manner as tallow. Wax may also be bleached by being kept in fusion in presence of animal charcoal, which retains all the colouring. On filtration the wax is obtained quite colourless. Certain oxidising agents, such as permanganates and dichromates in acid solutions and oxygenated water, give good results. Reducing agents, such as sulphurous acid, sulphites, hydrosulphites, &c., do not act upon the colouring matter of waxes. Chlorine removes the colour, but it is absorbed in equivalent proportions; the constitution of the wax is profoundly modified so as to render it unfit for use. The iodine figure of a pure yellow wax having been found 11.23 became after bleaching with animal charcoal 11.36; on bleaching with permanganate 5.80, and after treatment with dichromate 7.94 and in another sample 1.08.

On the Constitution of Benzo-pinacolline.—MM. Maurice Delacre.—The author contests the formula ascribed to this compound by Butlerow.

On a Characteristic Reaction of Cocaine.—A. J. Ferreira da Silva.—The author, after pointing out the objections to the physiological tests for cocaine, and the absence of a characteristic colour reaction, shows that it may be identified by the production of a certain odour. A small portion of cocaine or of one of its salts in the solid state, or the residue from the evaporation of one of its solutions in the water-bath, is treated with a few drops of fuming nitric acid, specific gravity 1.4, evaporated to dryness in the water-bath, the residue treated with one or two drops of a strong alcoholic solution of potassium. On mixing well with a glass rod, there is perceived a distinct odour like that of peppermint. This reaction is not merely characteristic but very sensitive. The author has been able to detect by this means a demidecimilligramme of cocaine.

Equilibria and Reciprocal Displacements of the Volatile Alkalies.—M. Berthelot.—Chemical statics is governed by two principles: that of maximum work, which merely takes account of the internal energies of the systems, and determines the exothermic reactions, whilst the principle of dissociation causes an intervention of the external calorific energies, and determines the endothermic reaction. The concurrence of these principles permits us to explain all chemical phenomena, and especially the reciprocal actions of acids and bases in a state of solution. If the original bodies or products experience no dissociation, and if they are in conditions favourable for the reaction, the magnitude of the heats evolved alone determines the phenomena. But if certain of the initial bodies or products are capable of dissociation, account must be taken of its existence and degree. If we have, e.g., a dissolved salt partly dissociated into free acid and base, the whole forming a system in equilibrium. Let us add another base; whatever may be

its relative force it will necessarily tend to appropriate a function of the free acid resulting from the dissociation of the antagonistic salt. Hence the primitive equilibrium will be disturbed, and a new portion of the original salt will be dissociated, regenerating some portion of acid which will be taken up in its turn by the second base. If the salt of the second base is capable of being eliminated by insolubility or volatility, we come to the application of the laws of Berthollet. If, on the contrary, it is soluble and remains in presence of the original bodies without experiencing any dissociation, it will tend to produce itself to ally in the liquids, the base whose salt is dissociated being definitely displaced by the base which forms a salt which is not dissociated. According as the second base disengages more or less heat than the first, the complete reaction may be either endothermic or exothermic. In the two cases it is equally the necessary consequence of the play of dissociation conjointly with that of the principle of maximum work; the former decomposes the salt into acid and base, and the second combines the acid as it is set at liberty with the other base. The author applies these principles to piperidine, pyridine, and aniline.

The Determination of Nitrogen as Ammonia by Means of Soda-Lime.—M. Berthelot.—The author performs such determinations in an atmosphere of hydrogen kept in the state of a slow current. The gas is previously purified by means of solutions of alkalis and salts of copper. The objects gained are that the hydrogen expels atmospheric oxygen contained in the tubes (which might burn traces of ammonia), reduces traces of manganates present in the soda-lime, and carries off the ammonia as produced, thus avoiding the slow decomposition produced at high temperatures.

The Acetylene Condensed by the Effluve.—M. Berthelot.—Acetylene thus condensed yields a very oxidisable product, which absorbs in a few weeks more than the fourth of its weight of oxygen. This product presents then the aspect of yellowish pellicles, which deposit a carbonaceous matter. If submitted to dry distillation it is abruptly decomposed, leaving abundance of carbon and evolving a large quantity of water mixed with acetic acid and acetonic liquids. Hence the condensation effected by the effluve is quite different from that effected by heat, which towards 400° to 500° yields chiefly benzene, which does not occur in the products of the condensation by the effluve.

Simultaneous Recognition of the Haloid Salts, and Especially of Chlorides, in Presence of Bromides.—G. Denigès.—(See p. 314).

MEETINGS FOR THE WEEK.

SATURDAY, 27th.—Royal Institution, 3. "Frost and Fire" (adapted to a Juvenile Auditory), Prof. Dewar, M.A., F.R.S.
FRIDAY, Jan. 2nd.—Quekett Club, 8.
Geologists' Association, 8.



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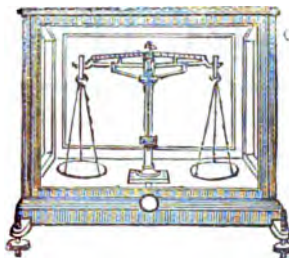
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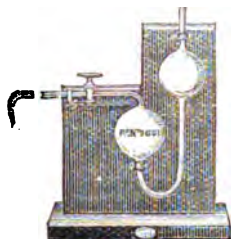
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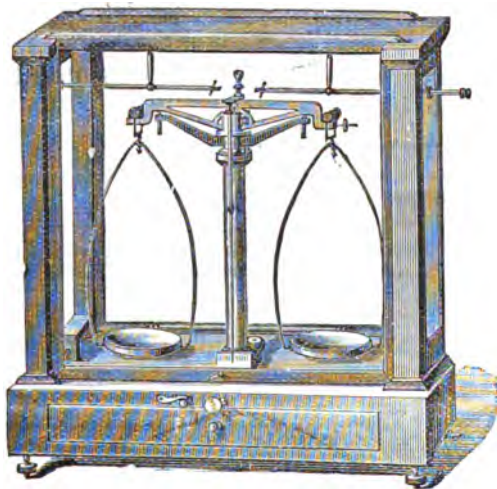


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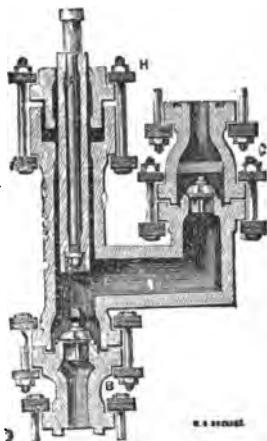
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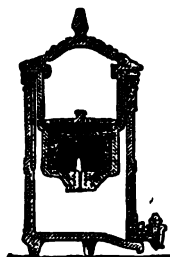
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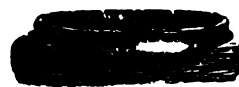
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